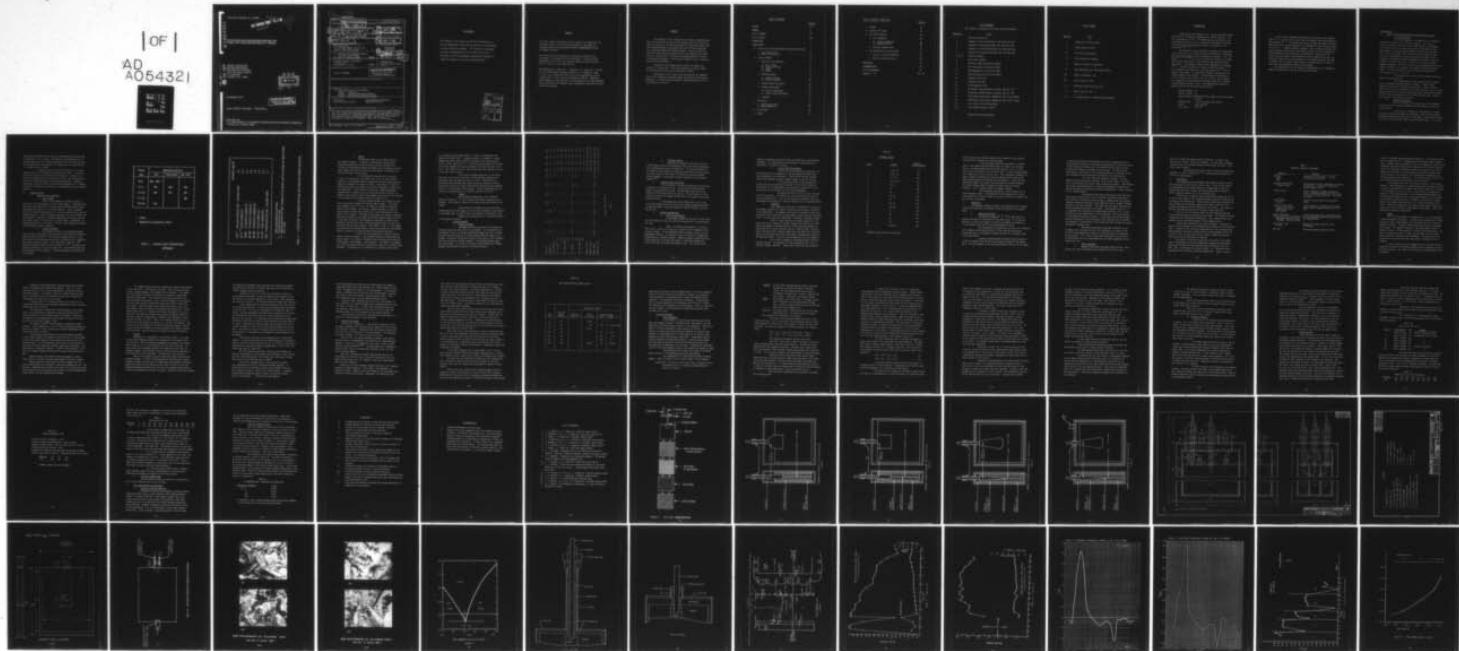


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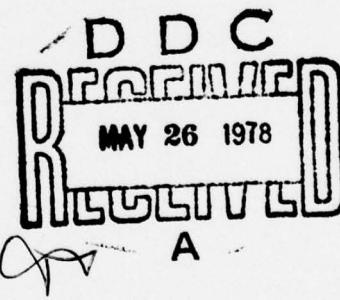
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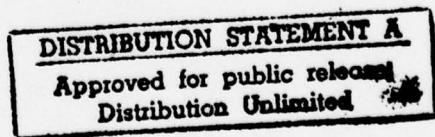
PRODUCTION AND ENGINEERING METHODS FOR
CARB-TEK® BATTERIES IN FORK LIFT TRUCKS

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FINAL REPORT VOLUME I – TECHNICAL

PREPARED FOR
U. S. ARMY MOBILITY EQUIPMENT RESEARCH & DEVELOPMENT COMMAND
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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report describes the technological development of the Carb-Tek® Molten Salt Li/Cl system toward prototype production for eventual assembly into fork lift truck batteries. Engineering developments, cost reductions, and pilot line operations are described and discussed. Significant failure mode is attributed to certain cell components. Seals are a problem. | | | | |

DISCLAIMERS

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents. The citation of trade names and names of manufacturers in this report is not to be construed as official government endorsement or approval of commercial products or services referenced herein.

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PREFACE

This final report, consisting of three volumes, was prepared by the Technology Center of ESB Incorporated under U.S. Army Mobility Equipment Research and Development Command (USAMERADCOM) Contract No. DAAK02-75-C-0035.

The objective of this program was to develop the manufacturing technology of the molten salt Li/Cl batteries. The goal was the demonstration of a molten salt battery meeting military specifications for fork lift truck applications.

Acknowledgement is made to Dr. T. Noveske, S. K. Jeung and C. Puckett for their development laboratory efforts, to J. Thompson, D. Mey, P. Struk, and E. Arnold for their pilot line contributions, and to R. Baker and S. Torreso for their engineering efforts. Additional acknowledgement is also made for the many persons at the ESB Technology Center and Standard Oil Company (Ohio) Laboratories who have willingly assisted the program.

SUMMARY

The objective of this program was to produce a demonstration fork lift truck battery from the cell system Li-Al/LiCl-KCl/C- TeCl_4 . Recent discovery of a significant internal failure mode coupled with seal leakage problems on the production sized 160-200 ampere hour cells prevented meaningful battery assembly. Partial corrections, based on failure mode, and improved seals show improved cell output and life. Maximum cell life cannot be obtained without a lithium ion conducting separator. Minor physical damage to such a separator would not be catastrophic.

Production size cathodes exhibit 160 to 210 ampere hour ratings at a 5 hour rate. Cells have exhibited as high as 198 AH. The present over-sized cells develop about 17 WH/lb.

Improvement in cell life can be realized with the substitution of non conductive retaining screens and lithium ion conducting separator. IR losses can be reduced by improved mounting of Li-Al alloy anode to cell wall.

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INTRODUCTION

Historically, the Standard Oil Co. (Ohio) researched molten salt batteries in 1962 and developed the Carb-Tek® battery. The work continued until 1971. The technology was transferred to ESB Incorporated starting in 1973. Background information concerning prior theoretical and laboratory studies are reported in the literature. (8, 9, 11).

The objective of this program is to develop the technology of the molten salt cell system Li-Al/LiCl-KCl/C-TeCl₄ to the point where low cost batteries could be produced in quantity. The Li-Al anode (1, 2, 3, 4, 10) is an alloy of about 16% lithium in aluminum. The LiCl-KCl electrolyte is the eutectic composition melting at about 355°C. The cathode is porous carbon impregnated with TeCl₄ (2, 5). Electrode separation is made by a BN fibrous mat (3, 6). Cell components are housed in a low carbon steel can (7) that is common to the anodes. A tungsten rod external lead connects the carbon cathode to the exterior. The operating voltage range is 3.2 to 2.4 volts with a lower limit of 1.0 volts. Cells operate at a temperature of about 420°C and develop 5 Whr/in³ of cathode volume between 2.4 and 3.2 volts. The demonstration battery is expected to have the following characteristics:

Nominal voltage - 36

Cut-off voltage - 30

Capacity when discharged from full charge to cut-off voltage -
- 720 Ahr

Recharge Rate - 1 hour to restore 80% capacity

Weight - about 1550 lbs.

Est. volume - 9.25 ft³

A pilot line was assembled and qualified to produce cells measuring about 4" x 5" x 5/16" and to obtain basic information concerning production type problems.^(8, 9) Engineering and process changes were made to enable a transition to the larger production size cathodes and cells measuring about 10" x 12" x 1". Numerous problems surfaced, such as external cathode lead seals developing leaks after a few thermal cycles; non or slow wetting of the BN separator by the electrolyte, discovery of a significant cell failure mode attributed to the presence of certain materials of cell construction; current collection problems in the cathode and anode; the need to produce the Li-Al alloy anode in house, and difficulties in ensuring that cells were completely filled with electrolyte.

Seal unreliability was in large part responsible for not assembling modules or batteries at the end of the contract period.

I. Investigation

A. Basic Cell and Battery Module Constructional Features

1. Cell Construction

The cell construction is essentially a rectangular carbon slab inserted into a series of pockets. See Figure 1. The first pocket is the boron nitride (BN) fibrous mat separator. A stainless steel wire screen pocket holds the BN pocket against the cathode. The pocket formed between the screen and the side walls of the low carbon steel cell can holds the anodes in place. This type construction was used during the early stages of the program, but BN wetting problems required an expansion of the cell thickness to ensure that electrolyte LiCl-KCl filled the space between electrodes. Additional screens were incorporated to hold the anodes in place and to increase the current collecting characteristics. The cell dimensions are over design in thickness only. Cells measure 13.5" x 11.25" x 2".

The electrodes are rated at 220 AH theoretically and 180 AH in actual practice.

Lead connections are made to the can body as anode and to a tungsten rod feed-through as cathode. Figure 2 shows features of early cells fitted with cold seals. Figure 3 shows features of the early Design MM-1 cell fitted with cold seal. Figure 4 shows features of the present Design MM-1 cell fitted with cold seal. Figure 5 shows the present MM-1 cell fitted with hot seal. Details are covered in the individual sections.

2. Module Construction

Full-size modules will contain four cells connected in parallel with 12 modules composing a 25 kW battery for fork lift truck purposes.

To gain basic information on the modules, a reduced sized unit has been designed and constructed. (See Figure 6 and the associated Legend number identified in the text.) The reduction is due in part to an insufficient supply of qualified hot seals. It is also

desirable to be able to test each cell individually and collectively as sub-units of 2 or 3 cells. The module must be encased in an insulated steel tray (8), fitted with heaters (18) for initial melting of the electrolyte, and exterior cell connections for accessibility (1 - cathode) and (2 - anode).

Included in the accessibility features are fill and exhaust valves (7) for flushing the housing with argon. A pressure relief valve must be attached to one of the vents. Venting is required to compensate for the pressure increase in the housing due to heating from room temperature to operating temperature. Heating is provided by two plate heaters (18) positioned between cells. Temperature can be indicated by connecting to a thermocouple inserted through gland (5).

B. Carbon Cathodes

1. Materials and Components

a. Basic Carbon

Early in the program the standard carbon material was FC-13 manufactured by Pure Carbon Company. Subsequent work has shown that grade PCB 30 x 150 mesh powder manufactured by Calgon Corporation was superior to the former material. Table I compares some of the physical characteristics. Note the higher active area for the PCB material. Table II compares laboratory cell tests results for each material. Note that the average laboratory cell output value at the present time is in the 5.8 to 6.2 AH/in³ range. Improvement in cathode conductivity is desirable. All MM-1 size cathodes are pressed and fabricated by Gaines Industries.

b. Current Collector

The current collector is an improved graphite cloth or paper type material manufactured by Union Carbide Corporation under the name of Grafoil^R. The improved graphite material is 30% more dense than that previously used and is referred to as a specialty high density cured grade GTB. The resistivity is about 6×10^{-4} ohm-cm as opposed to earlier value of about 9×10^{-4} . The density has increased from about 1.12 g/cc to about 1.56. No additional work has been performed in this category. Further improvement in conductivity is desirable.

| Carbon Type | REPORTED RESULTS | | |
|----------------|------------------|-----------|-----------|
| | ESB | PURE CARB | AM. INST. |
| PCB | 800 - 1400 ** | | |
| FC-13 | 540 | 400 * | 494 |
| FC-13A | 400 | 350 | 392 |
| FC-13B | | | 286 |
| MF-44I | 550 | | |

* Verbal

** Dependent on preparation method

TABLE I - SURFACE AREA COMPARISONS
(M²/GRAM)

| | | EXPECTED WH/IN ³ |
|------------------|---|-----------------------------|
| PCB | ++ (ESB OHIO PROJECT LAB) (CALGON CORP) | 5.9 |
| FC-13 | +++ (PURE CARBON CO.) | 5.5 |
| MF-441 | (STACKPOLE CARBON CO.) | 5.3 |
| MF-438 | (STACKPOLE CARBON CO.) | 4.8 |
| MF-439 | (STACKPOLE CARBON CO.) | 3.8 |
| FC-13A | * (PURE CARBON CO.) | 3.8 |
| FC-13B | * (PURE CARBON CO.) | 3.5 |
| PWA - PULVERIZED | (ESB LAB) (CALGON CORP) | 3.1 |

- + Other types tested but not listed
- ++ Various pressures used
- +++ Material obtained from ESB, Standard Oil Co. (OHIO), and Pure Carbon Co. stock on hand
- * 1975 Stock

TABLE II - A SELECTION⁺ OF CARBON TYPES AND THEIR RELATIVE POWER CAPACITIES

c. Header

The graphite header is an integral part of the cathode assembly. It serves as a mechanical and electrical connection between the current collector and the external lead. IR drops are encountered between the header and the tungsten external lead, between the carbon particles and the header, and between the current collector and the header.

In the transition from the No. 6 size cell, of about 10 AH capacity, to the MM-1 size cells, of about 200 AH capacity, it was assumed that the header must be only large enough to accept the tungsten rod without cracking. (See header in Figure 2.) Threading the parts was thought to improve the mechanical stability of the connection. It did not prove to be true. Numerous breakage problems made it evident that an improved design was required. In addition, the millivolt drop values between given points on the surface of the cathode and the header varied by a factor of 10.

To correct these problems, the tungsten rod was press fitted to the header for improved ohmic contact. The header was increased from 2 1/2" to 6" in length to essentially reach the center of the cathode. All corners, whether internal or external, were rounded to reduce the possibility of cracks developing in the header or the cathode. The width of the header was gradually increased from top to bottom as the length increased to prevent header pull-out. As the width increased, the thickness was decreased to reduce total graphite volume and the loss of working cathode volume; but the cross-sectional area was kept constant. (See Figures 5 and 7.) This design also permitted the cathode carbon to cover the surfaces of the graphite header to prevent any current by-passing the carbon electrode.

A millivolt drop technique is used as a quality control checking procedure. The procedure assisted in developing the header design. In practice, alligator clips are placed on the top and bottom edges of the cathode. (See Figure 8.) The header is connected to a positive current lead and to the positive lead of a millivolt drop indicator. The bottom clip is connected to a negative current lead

of a constant current power supply. A probe is connected to the negative millivolt lead. A constant current of 5 amperes is passed through the carbon and the probe is touched at the points desired. In No. 6 cells readings of 15 - 25 millivolts were obtained at various test points showing relatively consistent values for the small 10 AH cells. Early MM-1 cells were inconsistent and often registered values in the 400 - 600 mV range.

As the design changes were made, it was found that the values for the large 180 - 200 AH cathodes dropped to approximately the same range as the No. 6 cells. (See Table III.) The header design changes were effective and are standard practice. High density (1.82 g/cc) grade 2000 graphite manufactured by Stackpole Carbon Co. has been used for the header. Further improvement may be possible by substituting a full density graphite (2.25 g/cc).

d. Cements

Durite cement-Thermosetting Resin #SD5143 offered by Borden Co. is used to cement the cathode carbon particles together. This cement is converted to carbon during activation of the cathode.

Atlas Minerals & Chemicals Division ESB Incorporated Grade Furan 100 cement is used to bond the edges of the Grafoil^R to the header and, in certain cases, the carbon to the graphite cloth.

Cements are considered to be a significant factor in the internal IR total.

2. Cathode Assembly

a. Sandwich Concept

Throughout the major portion of the program, the sandwich concept has been used for the cathode. In this construction the graphite cloth is glued and sandwiched between two slabs or plates of carbon with the edges of the cloth exposed along the edges of the cathode. Occasional splitting was found to take place at the interface with the cloth due to unequal stresses. The exposed graphite edges were undesirable. To correct or alleviate these problems the cathode assembly was modified to achieve a unitized structure.

| | | | | | | | | | | |
|--------------------|-----------|-----------|-----------|---------|----------|----------|---------|---------|--------|---------|
| Cell Size | 6 | 6 | 6 | MM-1 | MM-1 | MM-1 | MM-1 | MM-1 | MM-1 | MM-1 |
| Cathode No. | 121 | 137 | 148 | 22 | 31 | 38 | 45 | 47 | 49 | 53 |
| Points/Reading | 9 | 9 | 9 | 9 | 9 | 9 | 23 | 23 | 23 | 23 |
| Avg. As Rec'd (1) | --- | --- | --- | --- | --- | --- | --- | 22.3 | 20.6 | 31.9 |
| " " " (2) | --- | --- | --- | --- | --- | --- | --- | 23.8 | 20.3 | 30.3 |
| Avg. Heat Treat(1) | --- | --- | --- | --- | --- | --- | --- | 18.7 | 17.7 | 15.1 |
| " " " (2) | --- | --- | --- | --- | --- | --- | --- | 18.4 | 18.1 | 15.0 |
| Avg. Impreg. (1) | 13.5 | 15.1 | 17.6 | 33.7 | 96.0 | 148.8 | 35.8 | 18.6 | 18.0 | 14.6 |
| " " " (2) | --- | --- | --- | --- | --- | 87.0 | 35.3 | 19.2 | 17.4 | 14.9 |
| Avg. Rod Insert(1) | --- | --- | --- | --- | --- | --- | --- | 21.3 | 19.3 | 16.6 |
| " " " (2) | --- | --- | --- | --- | --- | --- | --- | 22.6 | 19.6 | 17.7 |
| Range As Rec'd | --- | --- | --- | --- | --- | --- | --- | (7-45) | (7-30) | (14-76) |
| Range H. Treat | --- | --- | --- | --- | --- | --- | --- | (8-33) | (9-30) | (7-27) |
| Range Impreg. | (6.4-21.) | (7.6-22.) | (8.0-28.) | (23-43) | (74-115) | (76-160) | (10-64) | (8-31) | (9-30) | (6-26) |
| Range Rod Insert | --- | --- | --- | --- | --- | --- | --- | (11-31) | (7-29) | (7-28) |
| | | | | | | | | | | (6-21) |

MILLIVOLT DROP READINGS

TABLE I

b. Unitized Concept

Recessing the graphite cloth about 3/8 inch on each edge eliminated the exposure of the cloth to the electrolyte and strengthened the entire cathode unit. It was also possible to eliminate the glue between the graphite cloth surface and the carbon. The actual practice and process of forming the one-piece carbon cathode assembly is performed by Gaines Industries by proprietary methods.⁽¹⁴⁾

3. Cathode Carbon Activation

To be effective, the carbon cathode must be activated by heating in the absence of air. During the activation process cements are converted to carbon. Absorbed gases and moisture are effectively eliminated during the process. The activation is accomplished by heating the cathode to 850 - 950° C for several hours under moderate vacuum.

No improvement has been accomplished in this area. It has been noted that any portion of the cathode treated above 950° C or below the 850° C value has resulted in low AH ratings in the formation step.

4. Cathode Impregnation

a. TeCl₄ by Sublimation

An activated cathode can be used in a cell without the addition of TeCl₄ but the cell AH output will be approximately 70% less.

TeCl₄, as offered on the market, is listed as 99+% purity. Actual purity may be as high as 99.9+% depending on the source of supply. It was determined that purity was a factor in the enhancement obtained. An arbitrary value of 5 Whr/in³ of cathode was established as a minimum standard. Numerous cathodes containing TeCl₄ ranging from 99.0 to 99.99% were tested. The results showed that 99.7% purity was the minimum acceptable purity. The various purity

samples and standard processing stock were supplied by Great Western Inorganic. All impregnations were performed in sealed vessels at about 450° C for about four hours.

b. Li₂Te as the Active Agent

A short-term investigation was conducted into the possibility of introducing Te into the cathode by means other than impregnation by sublimation. Lithium Telluride was selected because the compound contains elements common to the cell system.

The high melting point of the compound suggested that the compound could be added to the initial carbon mix. Elimination of the impregnation step and precise control of Te concentrations were considered to be the prime advantages.

An equivalent amount of Te, as Li₂Te, was used for the experiments. The feasibility of substituting the Li₂Te for TeCl₄ was demonstrated. No large differences were noted in the cell performance curve tracings. (See the section on cell characterization.)

5. Formation

Each cathode is fitted with a tungsten rod to serve as the cathode lead and as a means of supporting the cathode in position in the electrolyte. The cathodes are cycled at constant current until they appear to be consistent in ampere-hours output and curve characteristics. At this point the charge mode is changed to constant voltage.

Table IV shows that the AH ratings ranged from 30 to 210 in the initial stages of the MM-1 program with the norm at 117 AH. Recent improvement to minimum values of 160 AH has been achieved by converting the 55 gallon formation tank to a heating bath, inserting small individual steel formation tanks that were previously lined with anodes, and charging with fresh electrolyte. Cathodes were formed in the individual tanks. (See Cell Failure Modes for basis of changes.)

As a result, cathodes are charging to about 160 AH on constant current. The cathodes are then increased to 180 - 216 on constant voltage charging. These results show that the minimum AH

TABLE IV

CATHODE HISTORY

| <u>Item #</u> | <u>Cathode*</u> | <u>Max. Ahr Rating/Cathode</u> |
|---------------|-----------------|------------------------------------|
| 1 | 12, 14, 17 | 30 |
| 2 | 16, 20, 23 | 153 |
| 3 | 7, 9, 18 | 210 |
| 4 | 19, 22, 24 | 164 |
| 5 | 10, 21 | 154 |
| 6 | 43 | 100 |
| 7 | 45 | 122 |
| 8 | 47, 48 | 146 |
| 9 | 49 | 160 |
| 10 | 50, 51 | 136 |
| 11 | 52, 54 | 145 |
| 12 | 53 | 160 |
| 13 | 57 | 100 |
| 14 | 55 | 145 |
| 15 | 59 | 156 |
| 16 | 56, 58 | 159 |

* Cathodes in each item run in parallel.

ratings required for battery operation are inherent in the cathodes and are to be expected as a routine product.

It has also been noted that the amount of electrolyte in the cathode during formation does not remain at a constant value. A formed cathode after discharge to about 1.0 to 1.5 volts will contain from about 4 to 4.25 lbs of salt. A fully-charged cathode will contain only 2 to 2.5 lbs of salt. This represents a movement of about 2 pounds of electrolyte from the cathode during charge and an equal amount entering the cathode during discharge. It has not been determined whether the change is proportional to voltage throughout the entire voltage range or whether it takes place at selected voltages. This is subject matter for another program.

This phenomenon represents a fluid pressure due to electrochemical action. The magnitude of this pressure and its possible negative or positive effect on the cell activity of a sealed unit has not been ascertained.

C. Separators

The separator problem has been, and continues to be, the most significant problem of the program in both the technical and economic areas.

1. Boron Nitride (BN)

The present separator^(6, 12, 15) is fabricated as a pocket (see Figure 1) from boron nitride (BN) roving. It is the only material, to date, that appears to survive the double environment of (1) the molten salts, and (2) the electrochemical fields.

BN is presently too expensive to be used in a production cell although the BN bonded BN mats or felts now being offered by Carborundum Corp. are expected to reduce the cost to a tolerable level in the near future.

A sample of the BN bonded BN material measuring about 1.5 mm in thickness and with 90% open volume was tested in the laboratory. For test purposes it was positioned against the face of the anode.

A previously tested and rated cathode was used to complete the cell. No discernable increase in IR drop was noted during 16 cycles of testing. The BN discolored slightly, held its shape during the test, but was broken during removal subsequent to the testing. This material was considered, on the basis of very limited testing, to be superior to the mats presently being prepared and utilized for cell construction.

BN is not free from technical problems. The mat formed from roving requires restraint in the cell to keep it in place. This is done by placing a mesh screen around the BN pocket. (See Figure 1) The screen, although effective, creates electrochemical problems and must be eventually eliminated or rendered nonconductive. (See discussion on Cell Failure Modes.)

BN separators and other insulating BN forms that have been placed within the cell structure almost invariably change from a pure white to a grey-black on the surface as viewed under a microscope. Scanning electron microscope studies (SEM) show small, randomly oriented growths of tellurium crystals. They appear to have grown from solution using hexagonal BN structure as a matrix. (See Figures 9 and 10.) It is suggested that there may be an appreciable solubility of Te in the electrolyte at the temperatures of cell operation. The steps leading to this condition may be as follows. As the cell cycles, some Te metal forms and dissolves in the electrolyte; then, when the cell is cooled, the hexagonal Te crystallizes on the nearest and most suitable nucleating (hexagonal) substance (BN).

Resistance measurements show that the BN has an exceedingly high resistance initially but decreases by a factor of 10^3 to 10^6 at room temperatures after 20 or 30 cycles due to Te deposited on the surface. It is safe to state that BN materials can be used on an interim basis for cell development but lack ideal properties for extended cell life.

2. Other Separators

Numerous substitutes have been tested to date. Many survive the static environment of the molten LiCl-KCl salts, but

fail or are found unsuitable during C/D cycling. In Table V the materials are listed. CaZrO_3 , for instance, can physically withstand the molten salts but becomes conductive after about 15 cycles. Silicates slowly dissolve.

The conclusion is that a solid, lithium ion-conducting separator, or solid electrolyte,⁽¹³⁾ is required before maximum cell life can be demonstrated.

D. Electrolyte

The electrolyte used throughout the program has been LiCl-KCl . The composition has varied from time to time. In the initial phases an approximately 50-50 weight percent of reagent grade salts were vacuum-dried with heat, melted, and then electrolyzed to remove residual impurities before use in the formation tank.

Difficulties in properly vacuum drying large quantities of salt in the initial stages of the program permitted the entry of moisture to the molten salt holding tank. Moisture that reached the formation tank was electrolyzed and removed, whereas the moisture retained in the holding tank remained to form hydrochloric acid vapors. The vapors invariably corroded through the 347 stainless steel tank walls.

Salt for cell filling was drawn from the formation tank and filtered through sintered stainless steel plates. The filtered salt was tinged with grey indicating contamination. This contaminant was considered to be a contributing cause to the leakage current.

Lithium metal producers have similar problems. Production of quality lithium depends on an electrolytically purified LiCl-KCl electrolyte. Purchase of salt from such production facilities eliminated the above-mentioned objections, reduced work load and equipment losses for the pilot line. The purified LiCl-KCl eutectic composition was purchased from Lithium Corporation of America.

An analysis of the salt volume used in the cells, the temperature of operations and the salt composition changes resulting from charge and discharge cycling indicated that the normally LiCl -rich salt used in production was more suitable. All recent work was performed with the lithium production composition. Figure 11 can be

TABLE V
MATERIALS TESTED AS SEPARATORS

| Material | Comments |
|---|--|
| BN Fiber Felts Mats | Resistant to electrolyte. Te metal crystallizes on surface. |
| BN Coated Reticulated Vitreous Carbon | Same stability as BN. Advantage in rigidity and handling. Difficulty in obtaining uniform deposit of BN. |
| Hercules Resin | Initial samples not stable in electric field. Subsequent samples were resistant to salts but became conductive. No longer available. |
| Zircar ^R Cloth ZYW-30A | Gradually deteriorated in the electric field. |
| Zircar ^R Yttrium Oxide Cloth as Tricot knit, Needled Felt, and Satin Weave | Cloth discolored. Appeared to be stable. Fragile nature deemed unsuitable for cell use. |
| Gaines Industries Various mixtures of Lepidolite, Spodumene, MgO and Calcium Zirconate. Special glasses. | Silicate base materials slowly deteriorate. Calcium zirconate becomes conductive without decomposition. |
| Ferro Corp. Glass RV-3303 | Appeared to slowly dissolve in the electrolyte. |
| MgO, BeO | The bonding agents appeared to fail. |

used to illustrate the above-mentioned analysis. A line drawn horizontally at about the 411° C temperature level intersects both liquidus lines. Assuming that the portion of the line between the liquidus lines represents the overall composition change of a cell during a complete cycle, then choosing the midpoint between the liquidus lines as the midpoint of a charge or discharge mode and dropping a perpendicular line to the Mol % axis results in an intercept corresponding to the lithium production cell composition. This ensures that no LiCl or KCl will precipitate during any portion of the C/D cycles.

This approach fits well with the basic nature of the C-TeCl₄ cathode. After impregnating a carbon cathode with TeCl₄ and inserting it into the electrolyte for formation the initial open circuit voltage is in the range of 2.8 to 3.0 volts. The 2.8 value is essentially a midpoint in the discharge mode. As the cathode becomes wetted with electrolyte and begins to store or discharge energy, the Li-Al anodes are increasing or decreasing in Li content. The additional lithium added to the anodes during charge or lost during discharge is minimized. Removing the cathodes at the same voltage range minimizes any build-up or loss of lithium in the formation tank anodes. Cells are designed to follow the same scheme.

E. Anodes

The Li-Al alloy anode is a complex entity. It is essentially a constant potential electrode. It permits the utilization of lithium with only a small (approximately 0.3) potential loss with respect to elemental lithium. It greatly reduces the safety hazards associated with lithium. For example, disposal of the alloy requires only immersion in water. The end product is soluble lithium aluminates. The heat of reaction with water is high, but no flames are in evidence unless some free lithium has been intermixed. The presence of free lithium does not necessarily mean that sparks or flames will be in evidence.

In this program most cell components are in the form of slabs, sandwiches or boxes to facilitate assembly and cell operation while in a vertical posture. Thus slab or sheet anodes are unobtainable on the open market.

Attempts to electrochemically form the anodes from aluminum sheet in assembled cells present two problems. The first is the necessary drain of LiCl from the electrolyte to alloy the aluminum with lithium metal. The second is the salt volume limitations that make it necessary to use thin aluminum in order that lithium alloy percentages of at least 8% can be realized.

A maximum cell life of about 150 cycles for such cells was reached when the aluminum was completely converted to small, discreet, unconnected, alloy particles.

The pressing of aluminum and lithium powders at room temperatures and then heating to immediately below the melting point of lithium resulted in a non-sintered loose alloy powder. Pressing of the powders at room temperatures without heat also results in alloy particles being formed in about 3 days.

The sandwich anode⁽¹⁰⁾ was developed to overcome the above problems. It was essentially a foil of lithium sandwiched between two sheets of aluminum in which reaction was initiated immediately below the melting point of lithium.

A few problems were noted for this anode preparation method. As the lithium attacks the aluminum to form the alloy, it often leaves a void in the center because it now occupies the same space as the aluminum sheets. In cell operation, this results in only one-half of the anode, the layer facing the cathode, operating as the anode. The other layer is essentially passive. In spite of this problem, a No. 6 size cell operated without failure over 313 cycles before being shut down.

Anodes formed by the sandwich technique generally display large crystals, visible to the eye, when viewed on the cross section.

These anodes were sufficiently brittle to suggest that the alloy formation should be performed in the place intended for use. This was done. Sandwiches were placed in cell cans, held in place by screening and then the can and the anode were heated to reaction temperatures. After cooling, the cell assembly was continued.

For formation tank anode use, baskets were made and spot welded to the tank walls. The tops were left open. Whole anodes and anode pieces, formed elsewhere, were dropped into the baskets. The baskets were wide enough to permit the placement or removal of anodes with laboratory-type tongs. This procedure permitted observations that were not possible previously. Over a period of months, it was noticed that the anode sections expanded and broke into pieces of about one inch square. With time these pieces subdivided further, and it was then apparent that the anodes would continue subdividing until a fine powder would result. It appears that without the benefit of a solid separator, the retaining screens would eventually become ineffective. One area in which a breakthrough is needed is the attachment of the anode to the cell can wall. There is an inherent IR drop of 0.15 to 0.30 volts in the present cell design at a current of 60 amperes. Much of this IR can be assigned to the lack of good ohmic contact. Reduction of the IR with respect to the anode contact will reduce the total IR of the cells. See the section on Screens for further discussion.

F. Screens

Screening is a requirement in the present system. It is used to hold the BN separator against the cathode and of the anode to the cell can wall. While the above arrangements are necessary for construction of the cell it is also deleterious to the life of the cell. In other words, the arrangement permits cell operation; but as the cell operates chemical side reactions take place that cause the reduction of tellurium ions to tellurium metal. (See section on Cell Failure.)

Early in the program, only one screen was placed around the BN-cathode assembly. To assist in making physical and electrical contact between the anode and the can wall, anodes were placed against the above-mentioned screen; and the entire unit was force-fit into the cell can. Neglecting breakage possibilities, the force-fit method was the means of forcing the anode against the wall to obtain a measure of electrical contact.

The compression technique often prevented salt penetration between electrodes and the fibers of the BN, thus many cells containing excellent cathodes could not function.

Widening of the cell to allow for sufficient electrolyte volume between electrodes resulted in anodes making contact at only two points, at the bottom edge and at the top edge. Cells operated but with high IR values. An improved electrical contact was essential.

Tight pockets made of screening stretched across the face of the anodes were employed. The four peripheral edges were spot welded to the can wall. This was an improvement as indicated by lower IR values. Further improvement was noted when an envelope of screening was fashioned and the entire back wall of the envelope was spot welded to the can wall. The procedure firmly contained the anode while providing a multitude of current collection points over both faces of the anode. Numerous spot welds provided contact between the screen current collector and the cell can walls and minimized the total IR drop. The total IR of the cell has been reduced to about 0.3 V with approximately 0.15 estimated as attributable to anode connections at 69 amperes.

Screen mesh sizing was also considered to be a significant problem. In the earlier portion of the ESB program and in the Sohio program, 100 mesh screening was used to act as a filter or retainer of anode particles that were assumed to appear early in cell life. The screen open area was about 30%.

With the discovery that one of the cell failure modes was directly attributable to the presence of the screens, it was realized that the particulate matter, for the most part, was finely divided tellurium and not alloy particles or carbon.

This result suggested that it was possible to improve cell performance and life by increasing the mesh openings. It was decided to use an opening in excess of the 24 mesh, 44% open area, reportedly used as a barrier for liquid lithium. Practical considerations indicated that an 18 mesh, 70% open area screen would be satisfactory. Following the same concept,

the larger opening wire mesh was also used around the cathode to reduce the total screen area available for lithium deposition and still be adequate for support of the BN separator. Following this theme, in conjunction with the Cell Failure Mode Model, a cathode was formed in the usual manner, obtaining about 100 AH. After the changes were made, the same cathode produced 162 AH.

Stainless steel screening was used in all cases because of the difficulty in obtaining standard steel screening that was free of copper, sulfides, etc. A recent cell post-mortem shows that the stainless steel appeared to have left a crust of nickel and chromium oxides in the salt adjacent to the anode screening.

The elimination of metallic screening with substitution of a ceramic or solid separator is most desirable.

G. External Cell Leads

The cell can is anodic (-). Any suitable connection to the can body, compatible with physical design, appears to be sufficient for electrical purposes. Connecting from the cathode, through the cell can wall, to the exterior is a major problem. Two approaches have been followed: (1) cold seal and (2) hot seal.

The cold seal is a device designed to affect a seal against moisture and air at temperatures less than the cell operating temperature. Figure 12 is a diagram of such a seal. Other, similar devices are being utilized.⁽¹²⁾ The tube extension is designed to allow the seal itself to be beyond the confines of the cell test oven or heating medium.

Cold seals involving the Conax^R coupling were found to be satisfactory for the small No. 6 size cells involving an 1/8" diameter tungsten lead and a 1/2" coupling. Many units sealed about 1970 are still effective.

Scaling up to a 3/8" diameter tungsten lead and a 3/4" coupling resulted in erratic behavior. These results are presented in a historical manner. Numerous cells were tested at the Cleveland, Ohio location for leaks using helium. Subsequent to passing the leak

test these cells were cycled and were found to be satisfactory, were then cooled to room temperature, crated, and sent to Ft. Belvoir, Virginia, for further testing. The results obtained at Ft. Belvoir seldom verified the Cleveland results with respect to AH, and relatively short cell life was the rule. Room temperature resistance readings were found to be unexpectedly low. Values as low as 7.0 ohms were noted. The female portion of the Conax^R fitting was found to be only finger tight. Units were considered to be leak-tight and connection-tight before shipment.

Study of the problem revealed that a helium leak-tight system would remain leak-tight during initial heating and subsequent cycle testing, but cooling down could result in leakage. Torque values of about 70 ft-lbs prior to the initial heat cycle were required to prevent leakage throughout the test. Retorquing to 70 ft-lbs was required after each cooling. No assurance of leak-tightness could be given after the fourth retightening due to the extruding of the rubber gasket seal beyond its elastic limit.

When these results were applied to a regular production type MM-1 cell, the room temperature resistance values were markedly higher in two of the three cells after salt-fill while one of the three (#138) retained a high resistance after 66 cycles as shown in Table VI. It is believed that a significant result was obtained, but further testing is required to confirm the conclusion. Adequate hot seals will eliminate the problem.

It is highly probable that a large number of cell failures were caused by moisture penetration through inadequate seals, causing low resistance values, attack on cell walls, and eventual salt leakage.

Hot seals are seals designed to operate at cell temperatures with the external leads sufficiently long to permit bus bar connections within the cell modules and from module to module to form a battery.

None of the units supplied have survived thermal cycling although the initial leak rates were in the 10^{-8} and 10^{-9} cc-atm/sec. Examination of seals after failure revealed good bonding between the glass and the tungsten; no cracks or crazing in the glass, but possible

TABLE VI

ROOM TEMPERATURE RESISTANCE VALUES

| CELL NO. | 70 FT. LBS. TORQUE APPLIED | RESISTANCE IN OHMS | | | |
|-------------|----------------------------------|-----------------------|--------------------|---------------|-------------|
| | | PRIOR TO SALT FILL | AFTER SALT FILL | AFTER CYCLING | |
| | | | | NO. | OHMS |
| 63 | No | | 4,800 | -- | -- |
| 119 | No | | 40 | 40 | Cell Leaked |
| 98 | No | | 10,121 | -- | -- |
| 127 | No | | | 22 | 355 |
| 129 | Yes | | | 100 | .35 |
| 135 | Yes | | | 145 | 1.7 |
| 138 | Yes | | 9,000 | 66 | 23,000 |

separation of the glass from the KOVAR tubing. It was an unexpected point of failure but may be corrected by a change in the grade of glass employed to a multigrade and to recheck the KOVAR cleaning procedure. The additional costs will be minimal. An appropriate seal can ensure moderate cell performance and life until a lithium ion conducting solid separator can be developed. Figure 13 shows the hot seal concept. The BN prevents salt penetration and the glass provides an air seal.

H. Cell Failure Modes

1. Cell Components

A cell model is presented that explains the failure mode, the gradual increase in holding current requirements, and the appearance of tellurium metal crystals in the separator. The failure mode is a direct consequence of the internal cell design. The sequence of events that cause the above problems are actually symptomatic of electrodeposition of lithium metal on all exposed steel components primarily during the charge mode. A subsequent chemical reaction produces the undesirable effects. Certain design changes have been made to partially correct the problem, while others are indicated but not attainable, at this time. A significant improvement in cell life is anticipated as each of the appropriate changes are made.

The background of the early cell system is presented again to assist in the understanding of the presentation.

Cell components are listed below including pertinent remarks. Refer to Figure 14 for a visual concept of cell geometry.

Electrolyte - LiCl-KCl, 5% LiCl rich, from Li production cells
saturated with Li (Li solubility approximately 0.1
mol % of .01 wt.%).

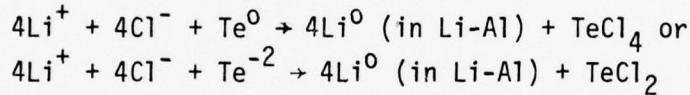
Cathode - Porous carbon impregnated with TeCl_4 , completely surrounded with fibrous BN mat of >90% open volume. BN surrounded with 28 mesh screen approximately 50% open area. Screen is used to hold BN in place. Screen does not contact cathode.

Anode - High density Li-Al alloy (16% Li) fastened to cell wall by 100 mesh screen approximately 30% open area. Screen is used to hold any particulate anode material in the screened area.

Cell Can - Low carbon steel. Anodes cover most of the large dimensional area. All other areas are exposed.

The expected cell mechanism is as follows:

On charge, the electrolyte tends to move out of the carbon electrode. The LiCl portion of the electrolyte yields an equivalent amount of lithium metal at the "anode" to alloy with the Li-Al electrode. An equivalent amount of tellurium increases in oxidation state.



On discharge, the reverse actions take place.

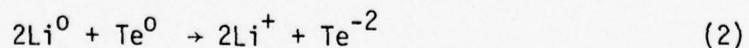
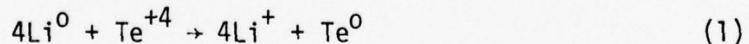
Generally, cells tend to show an increase in AH/cycle, reach a maximum value, and then slowly decrease. The holding current decreases and then gradually increases. Dissected cells show a general distribution of well-defined, randomly distributed tellurium metal crystals. The Te crystals appear to be concentrated in the BN separator.

Believing that the reactions taking place between electrodes and in the BN separator should also take place on the carbon particle surfaces within the porous carbon electrode, an attempt was made to find Te particles. A scanning electron microscope was used by A. Simon of the Naval Research Laboratories to search for minute crystals of tellurium in the cathode body. Such crystals were found.

With the above information it was possible to develop the following model:

On charge, the lithium ion (Li^+) is reduced and electrodeposits on all negatively charged surfaces. These surfaces include the Li-Al alloy electrode and all exposed steel surfaces, such as, the steel can, the screen around the anode (found in recent cells), and the BN retaining screen around the cathode. In the case of the screens, the deposition takes place on the surfaces facing the carbon electrode. (See Figure 14.) It must be remembered that the screen against the Li-Al is mechanically and electrically connected to the can wall. The screen around the cathode is not mechanically connected to any conductor. Under the influence of the electric field, during charge/discharge, opposite surfaces of the cathode screen will have opposing charges and, therefore, can be considered as an intermediate electrode. The deposition of lithium on the above surfaces is essentially proportional to the exposed area; therefore, most of the total lithium deposits on the Li-Al alloy electrode and is assimilated. Lithium deposited on the steel surfaces that remains in place will be available for the discharge cycle and at a 0.3 volt higher potential (See Diagram, Figure 14.)

The free lithium on steel is unlikely to remain in place, particularly if an appreciable thickness develops. The metal will tend to release, tend to float to the top of the cell. During the released time the Li^0 is reducing tellurium. The Te can be in any oxidation state from zero to plus four (or six) as shown in the equations:



In equation (2) the product could be Li_2Te which is slightly soluble in the electrolyte. Conjecture at this time is that the Te^0 of equation (1) is soluble to a large extent.

The solubility of Te metal in the melt is based on the fact that (1) no concentration of metal particles or crystals has been

found at the bottom of the cells, although the specific gravity of Te is about 6.25 as compared to 1.65 g/cc for the electrolyte; nor are there any indications of a concentration gradient from top to bottom of the cell; (2) the tellurium metal found in dissected cells has been highly crystalline (hexagonal) and randomly oriented suggesting a normal crystallization from solution upon the favorable, hexagonal, boron nitride separator. See Figure 9 and 10 for SEM photographs taken by A. Simon of NRL.

No needles of tellurium metal are believed to exist in the cell at the operating temperatures of 410° - 440° C since no oriented needles have been found or have been indicated in actual photographs. (See Figure 9 and 10.) Any needles that might conceivably grow from the surface of one electrode and reach the other electrode, or the screens, would certainly melt like a fuse link. No globs or pools of Te have been found upon examination. It is also obvious that Te^0 rather than Li_2Te is formed since only hexagonal Te crystals are found. Li_2Te is cubic. In a static test, unagitated tellurium metal dissolved in the electrolyte being maintained at 400° C to the extent of 0.007 grams metal per gram of electrolyte over a period of 18.5 hours. No attempt has been made to determine whether the figures represent saturation.

Referring to Figure 14, it is obvious that the deposition of lithium on one side of the intermediate screen should result in the deposition of chlorine gas in the initial cycles; but as the Te concentration spreads and increases throughout the electrolyte then Te should deposit on the surface.

Returning to consideration of the deposition of lithium metal on the screens, it is apparent that the screening around the Li-Al alloy is too fine (100 mesh) to allow the liquid metal to pass through, to contact the alloy, and to be absorbed. Screening finer than 24 mesh acts as a barrier to liquid lithium. The screening around the BN has been 28 mesh and is also a barrier, causing liquid lithium

to stay in the vicinity of the BN separator. It is obvious that the expected increase in lithium concentration in the Li-Al alloy as a result of charging is less than necessary because of the small losses due to the side reaction. Repeated cycling gradually reduces the percentage of lithium in the Li-Al alloy. This effect is irrespective of any loss of usable lithium due to formation of pure β crystals or particles in the alloy.

On discharge, essentially reverse reactions take place. Lithium from the Li-Al alloy enters the electrolyte as Li^+ ion. Lithium previously deposited on the steel parts does the same. (Refer to surfaces facing the carbon electrode in Figure 14.) Surfaces facing the Li-Al, such as the BN retaining screen, will vary in their reaction. In the initial cycle or so there are no tellurium ions in the electrolyte so chlorine evolves on the surface. As Te ions permeate the electrolyte it is reasonable to expect the deposition of Te on the surface, subsequent oxidation to a higher state, and the dissolution as a chloride. All of the Te does not convert to the higher oxidation state chloride.

At the carbon electrode surface and interior, the tellurium is oxidized to higher positive valencies.

During discharge the electrolyte tends to migrate into the cathode carrying with it some dissolved tellurium.

The detrimental effect after a given cycle is the loss of a small, but finite, portion of the lithium of the Li-Al alloy.

Considering the fact that the BN is immediately adjacent to the carbon cathode and the retaining screen, it is necessary to realize that the electrolyte at the immediate surfaces will be influenced by the polarity of the steel screen and of the carbon cathode. Each surface will be of opposite polarity. These facts are important when it is realized that the BN essentially prevents any agitation or stirring actions. Electrolyte composition changes can be expected to be maximized.

An additional problem is caused by lithium floating to the top of the cell and providing an electronic path or bridge between electrodes. This can explain lowered cell ohmic resistances at room temperatures.

Black particulate matter found in the electrolyte can be attributed to a large extent to finely divided Te metal or Li_2Te rather than carbon particles.

Cell failure can be explained by the above, which indicates that short cell life is a result of physical cell parameters rather than the basic cell system.

a. Corrective Measures

Correction of the defects must be accomplished in stages. The first stage involves two parts. Part 1 is the increase in mesh screen openings to greater than 24 mesh. This allows lithium to pass through and reduces the total surface available for the intermediate electrode syndrome. The second step is the covering of all exposed cell wall surfaces with Li-Al alloy. It will maximize the capture of lithium produced by deposition and the free lithium that floats to the top.

The second stage is the modification of the BN separator to permit about an 80% reduction in screen requirement, reduce total BN requirements and improve uniformity within the separator body. This can be accomplished by using the Carborundum Company's new BN bonded BN felt. It has a degree of self support which will allow the reduction in total screen required. It is very thin, about 1.5 mm thick, and may reduce or eliminate the build-up of Te metal within the structure. Laboratory testing, to substantiate this premise, is in progress.

The third stage is the elimination of the metallic screens. The means by which this stage can be accomplished has not been completely defined and remains as a significant problem. Metallic screens conceivably could be replaced by non-conductive screening without detrimental effects.

The fourth stage can eliminate all of the above-mentioned design or cell construction failure modes including the reduction of Te species by Li. It entails the use of an ionic solid separator based on lithium.⁽¹³⁾ Such a separator is usually designated as a solid electrolyte. An analogous example is beta alumina that is used in the sodium metal systems.

Such an approach is not free from problems, but it must be mentioned that there is a distinctive difference between this system and many others. The failure of a "separator" in competing systems is immediately disastrous to the cell and may be unsafe for personnel in the area. The same situation for the cell system under study only reverts to the situation being presently experienced. It is the opinion of the author that the discovery of a suitable, highly ionic, conducting separator will result in a practical cell of exceptionally long life and high power density.

b. Supporting Data

A few experiments have shown that a large improvement in AH ratings can be expected with only a few of the earlier mentioned changes being made. The improvement has been demonstrated as completed cells in subsequent testing. Cathode No. 109 was formed while facing the normal set of 2 anodes. Three cycles gave 85, 108, and 107 AH. The cathode was removed. Aluminum sheets were placed on the ends and bottom of the tank to mask the exposed steel portions. (The concept was to prove that Li was not only depositing on the anode but was also depositing on the exposed steel. If true, there would be evidence of alloy formation on the surface of the aluminum.) The cathode was returned to the tank. A slight change in the charge curve was noted. The voltage curve had a lesser slope. Three cycles -- 95, 125, and 110 AH were noted. Not a large improvement in AH. The aluminum sheets were removed and were found to be alloyed with lithium, with one portion showing a few holes. The holes were probably due to complete alloying of the thin aluminum sheets and a subsequent breaking away, due to a higher concentration of current at that point.

A new mini-formation tank was prepared with anodes covering about 85% of the interior steel walls. The same cathode was inserted. After 4 cycles the AH rating rose to 162. The cathode was removed after 30 seconds at O.C.V. It appeared to be at least as clean as previous cathodes after being subjected to a 4-hour O.C.V. settling period. At this writing, several cathodes have exhibited AH values of 216.

Cathode No. 129 produced the following data in formation in which anodes covered 80-85% of the available steel areas. See Table VII (next page).

As a completed cell, including 80-85% steel coverage, 18 mesh screens, and fresh electrolyte salts, the following data was generated:

TABLE VIII
DATA ON CELL NO. 129

| <u>Cycle #</u> | <u>Charge Mode</u> | <u>AH</u> | <u>Comment</u> |
|----------------|--------------------|-----------|---------------------------|
| 1 | Const. Current | 49 | BN not completely wetted |
| 4 | Const. Current | 73 | Changed to const. voltage |
| 8 | Const. Voltage | 202 | --- |
| 12 | Const. Voltage | 185 | --- |
| 16 | Const. Voltage | 179 | --- |
| 20 | Const. Voltage | 94 | Controller Problem |
| 24 | Const. Voltage | 194 | --- |

This data show that it was possible to reach the design AH criteria for batteries by taking advantage of the Failure Model without changing any methods, procedures, or stock materials. It also represents a major improvement over the results previously obtained as cells. Cell 129 has continued to operate. It shows that the failure mode gradually becomes significant, as shown in Table IX below and in Figure 15.

TABLE IX
DATA ON CELL NO. 129 (Continued)

| <u>Cycle No.</u> | <u>37</u> | <u>43</u> | <u>57</u> | <u>64</u> | <u>74</u> | <u>80</u> | <u>91</u> | <u>100</u> |
|------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|------------|
| <u>AH</u> | 180 | 177 | 163 | 150 | 140 | 134 | 114 | 92 |

TABLE VII
DATA ON CATHODE NO. 129

Initial voltage in formation = 2.86
Constant Current Charge/Discharge = 36A (3 cycles)
Constant Voltage Charge = 36A (2 cycles) then inc. to 60A
AH Rating for next 4 cycles = 180
Removed from formation tank and cooled to determine whether
thermal cycle affects capacity. Returned to Tank for 3 cycles.

| <u>Cycle No.</u> | <u>10</u> | <u>11</u> | <u>12</u> |
|------------------|-----------|-----------|-----------|
| AH | 151 | 175 | 182 |

(Cathode removed for cell assembly)

Cell No. 135 is given as an example of a cell short of sufficient anode stock, but which is operational, as shown in the Table below and in Figure 16.

TABLE X
DATA ON CELL NO. 135

| Cycle No. | 1 | 18 | 34 | 48 | 62 | 76 | 92 | 107 | 117 | 134 | 144 |
|-----------|---|----|----|-----|-----|-----|-----|-----|-----|-----|-----|
| AH | 8 | 30 | 80 | 108 | 120 | 127 | 126 | 126 | 124 | 114 | 112 |

To add further substantiation to the model, the following experiments were conducted on small one cubic inch cathodes.

(1) A cell was assembled coupling sheet steel (-) and a discharged carbon cathode (+). The initial O.C. voltage was 1.5 volts. As the cell was charged the cell voltage rose to 3.0 as lithium metal deposited on the steel, thus converting the steel to a lithium electrode. This shows that lithium metal deposits on the steel parts of the cell during the charge mode when opposed by a carbon cathode.

(2) A second cell was assembled coupling sheet steel (-) to a LiAl electrode (+). Lithium deposited on the steel. The potential difference was 0.30 volts. This experiment shows that loss in potential between LiAl and Li is essentially 0.3 volts. It also shows that lithium can deposit on steel parts, such as the screen area that faces the alloy electrode during discharge.

(3) Lab cells having larger areas of exposed steel indicate larger tellurium concentrations in the electrolyte. Additional experiments are needed to confirm the results.

2. External Cathode Leads

See the previous section on seals for a discussion on cell life difficulties due to seal failures.

I. Cell Characteristics and Studies

1. Li_2Te as a Possible Additive

Differential capacity measurements on carbon cathodes containing either TeCl_4 or Li_2Te indicate similar electrochemical behavior (Figures 17 and 18). These figures suggest that Li_2Te could be used in place of the present TeCl_4 additive. Open cells containing Li_2Te as an additive to the carbon cathode substantiate these findings. The major advantage in using the telluride in place of tellurium halide is in the elimination of the vapor impregnation step. Since Li_2Te has a high melting point it can be added

to the carbon granules during cathode fabrication. Precautions necessary for the safe handling of tellurium will be necessary. A possible disadvantage may be an increase in cost per unit of tellurium.

2. Tellurium Characteristics

Cycling a cathode in consecutive Te-free electrolyte pots showed a relative capacity stability in each pot after an initial drop. Capacity levels consecutively decreased, however from pot to pot (Figure 19). The lower power level in pot IV is attributable to stress cracking in the cathode. Analytical results of tellurium concentration in these pots is shown in Table XI. These results suggest that soluble tellurium in the electrolyte may be necessary in order to achieve the rated capacity. However, tellurium present in the elemental state will lead to an increase in final holding current and gradual capacity deterioration. (See Cell Failure Mode.)

The importance of the final charge voltage in achieving an optimum capacity is seen in Figure 20. The graph illustrates a doubling of the AH capacity of the cathode, 3.5 to 7.0 watt-hours/in³, while the final charge voltage was changed from 2.00 to 3.32 volts. No significant changes in the holding current were noted. A high final charge voltage is also necessary for proper cathode conditioning in the formation step. Failure to condition the cathode in the formation step results in an unusually large outgassing of a cell during the early cycles of finished cell.

TABLE XI
Te CONCENTRATIONS - CONSECUTIVE ELECTROLYTES

| <u>Electrolyte Container</u> | <u>% Te</u> |
|------------------------------|-------------|
| No. I | 0.044 |
| II | 0.035 |
| III | 0.031 |
| IV* | 0.019 |

* A thermally stress cracked cathode became evident upon changing to the fourth pot of tellurium-free electrolyte.

CONCLUSIONS

1. Cathode and cell AH ratings of over 200 have been produced.
2. Cathode minimum Ah rating of 160 Ah has been achieved.
3. A major cell failure mode that is inherent in the cell material of construction has been discovered.
4. Total correction of defects in (3) above cannot be accomplished immediately.
5. Many cell failures can be attributed to improper or inadequate cathode feed through seals.
6. Evidence indicates a large solubility of tellurium metal in the LiCl-KCl electrolyte.
7. Undesirably high holding current values are inherent in the present cells and may not be correctible without the use of a solid Li ion conducting separator.
8. Holding current values of the larger, 120 in³ cathodes have been reduced to the values obtained with the smaller 20 in³ cathodes.
9. Bn bonded BN appears to be worthy of continued study as a suitable separator for cells in early production.
10. Tellurium tetrachloride must exceed 99.7% purity.
11. Lithium telluride is an alternative impregnant and can be introduced at the time of cathode fabrication, thus eliminating the costly impregnation step.
12. Grade PCB carbon material obtained from Calgon Corporation is adequate for cell purposes.

RECOMMENDATIONS

1. Complete development of the hot seal.
2. Replace wire screen components with a non-conductive screen structure. This action can increase cell life significantly.
3. Develop lithium ion conducting solid electrolyte separator. Ultimate success can be obtained by introducing a lithium ion conducting solid separator. A minor failure of the separator body would not be catastrophic. This substitution would not only reduce the leakage, or holding, current problem to a minimum but would also permit a 3- or 4-fold increase in WH/lb.

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2. R. Rightmire, et al, U. S. Patent No. 3,567,516, dated 3/2/71.
3. H. Adams, U. S. Patent No. 3,428,493, dated 2/18/69.
4. J. E. Metcalfe, et al, U. S. Patent No. 3,762,954, dated 10/2/73.
5. R. Rightmire, et al, U. S. Patent No. 3,770,506, dated 11/6/73.
6. T. B. Selover, et al, U. S. Patent No. 3,816,242, dated 6/11/74.
7. T. Hacha, U. S. Patent No. 3,645,792, dated 2/29/72.
8. J. C. Schaefer, "Characteristics of the Molten Salt Carb-Tek^R Battery," Paper No. 750148 SAE Congress, Detroit, Michigan, 2/26/75.
9. J. E. Metcalfe, "Production and Engineering Methods," AD 006 548, Contract DAAK 02-73-C-0493, December 1974.
10. J. C. Schaefer, U. S. Patent No. 3,981,743, dated 9/21/76.
11. J. C. Schaefer, "Production and Engineering Methods for Carb-Tek^R Batteries in Fork Lift Trucks," Interim Report dated March 1975 - March 1976.
12. T. B. Selover, Jr., et al, U. S. Patent No. 3,472,701 dated 10/14/69.
13. E. S. Buzzelli, U. S. Patent No. 3,506,491, dated 4/14/70.
14. F. W. Gaines, U. S. Patent Approved, Awaiting Issue
15. T. B. Selover, Jr., et al, U. S. Patent No. 3,510,359, dated 5/5/70.
16. C. L. Mantell, "Electrochemical Engineering," p. 422, 4th Edition, McGraw Hill (1960).

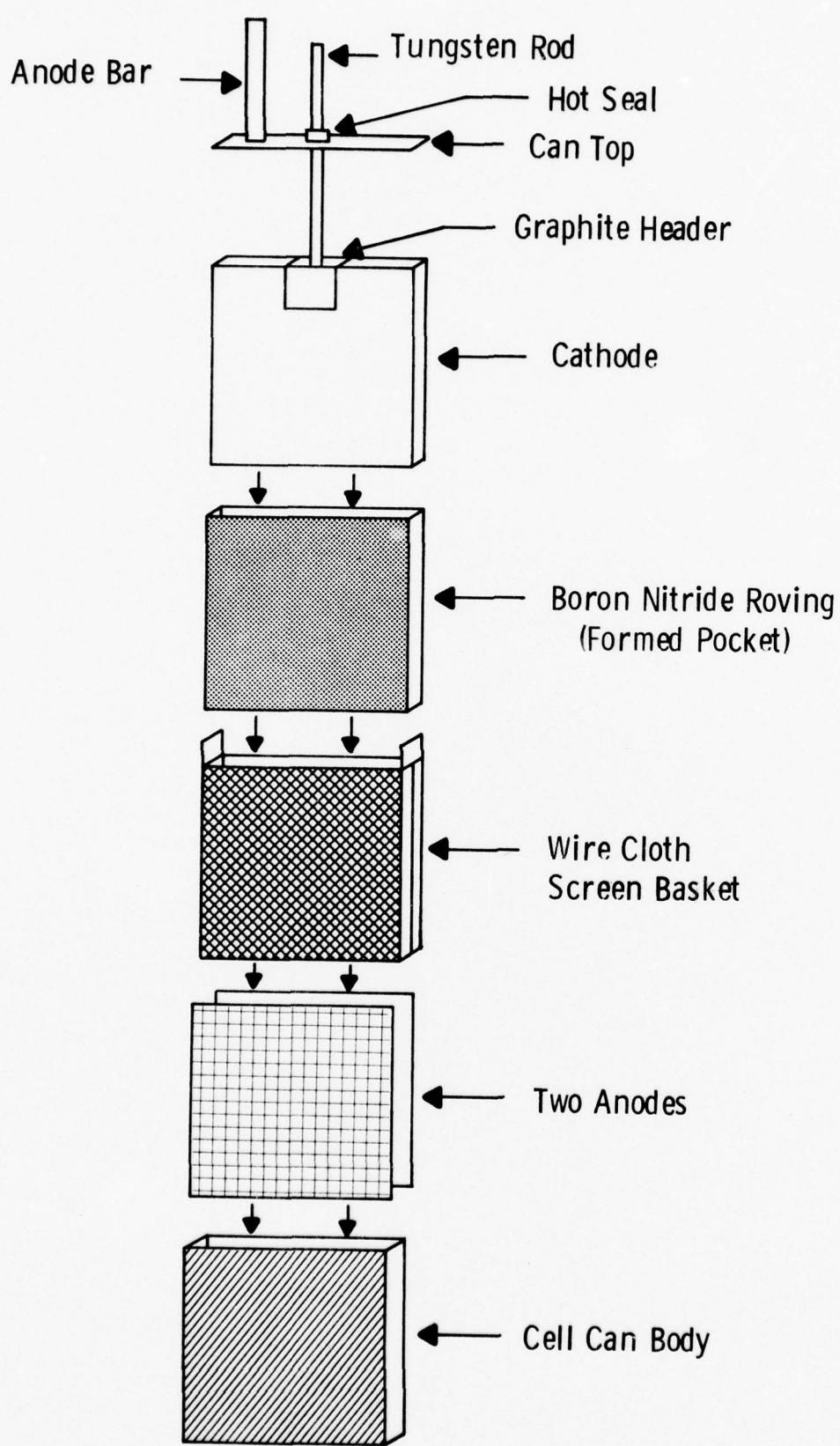
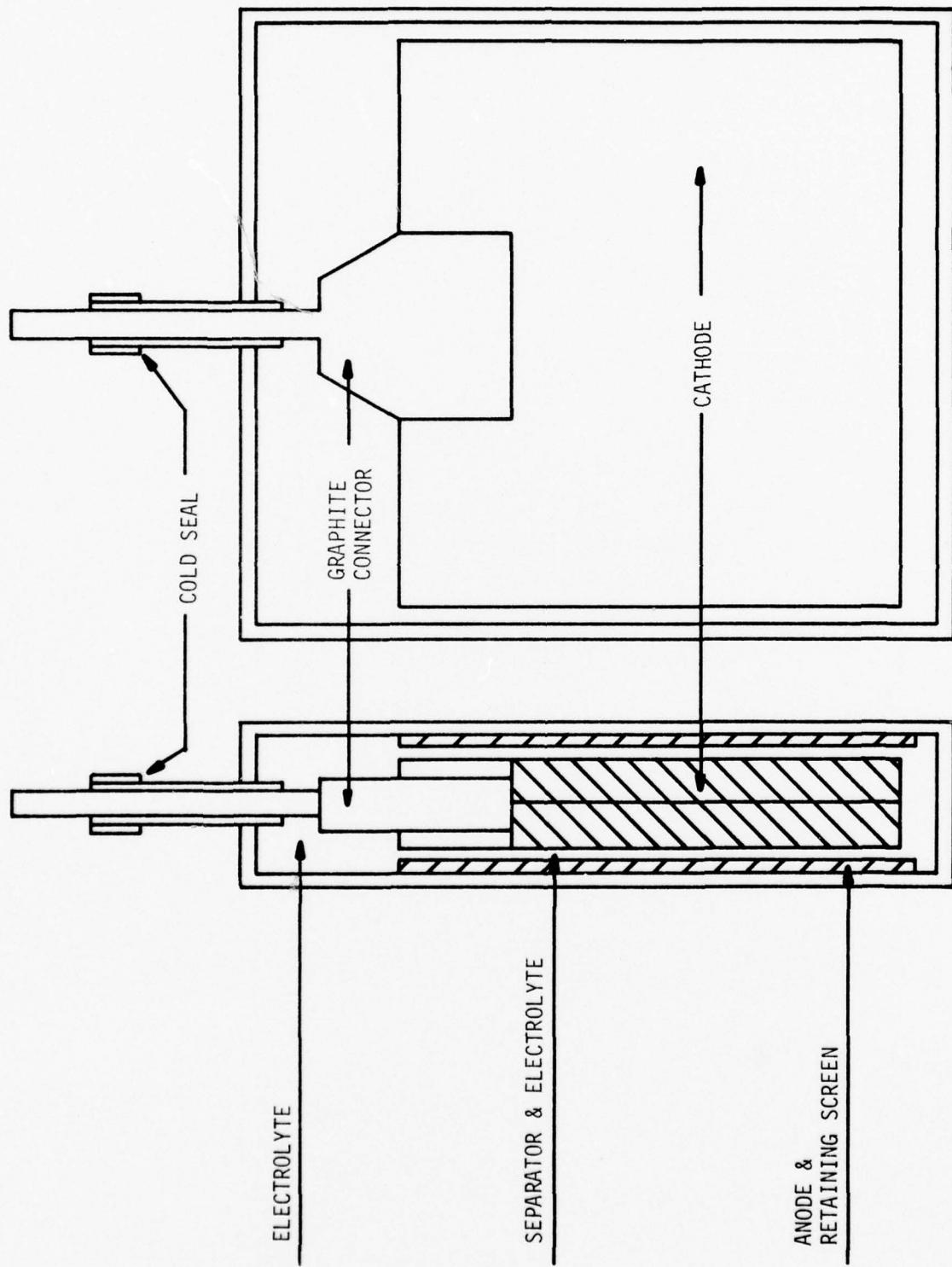
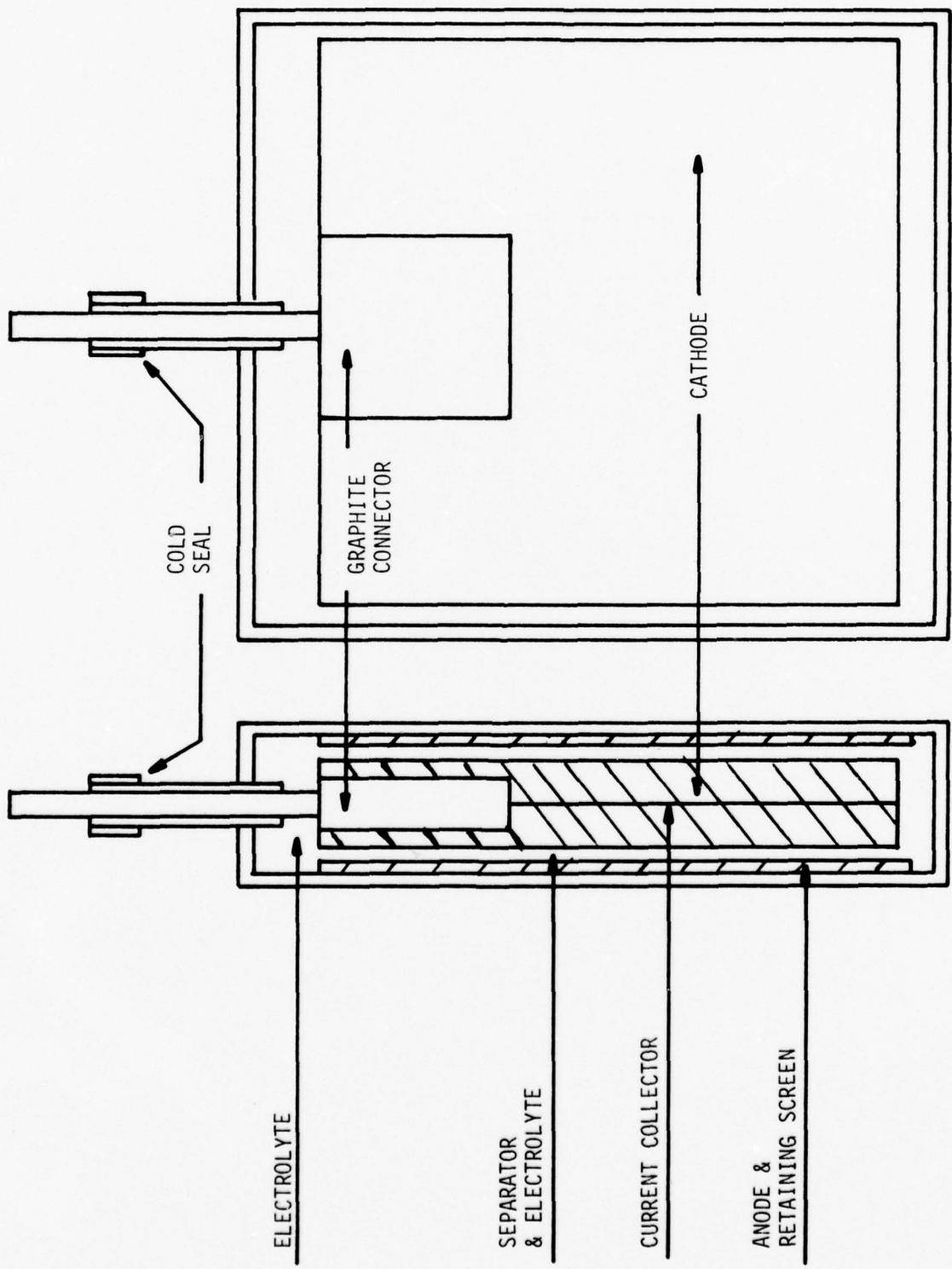


Figure 1 - ESB CELL CONSTRUCTION



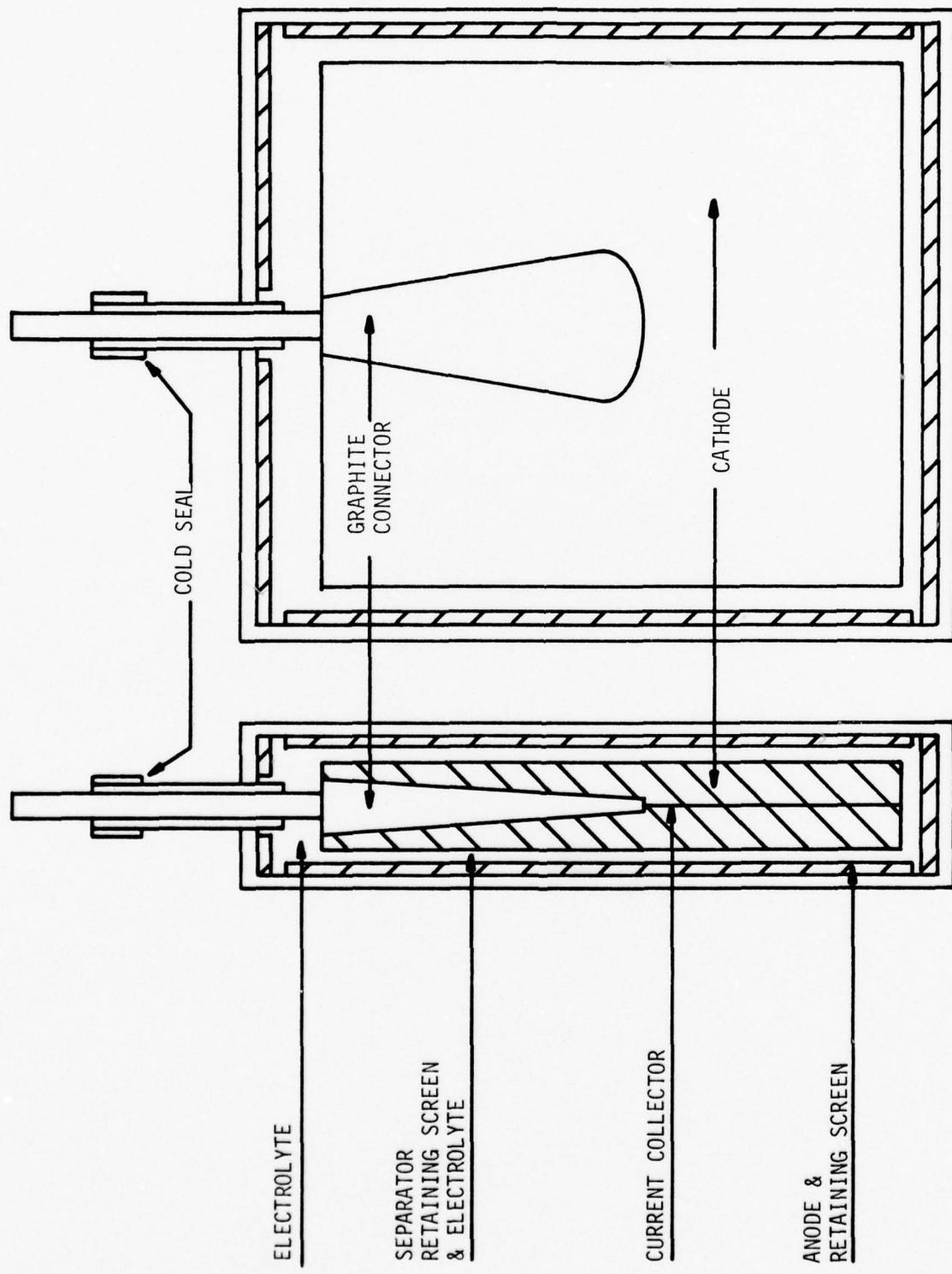
SCHEMATIC OF DESIGN No. 6 CELL WITH COLD SEAL

Figure 2



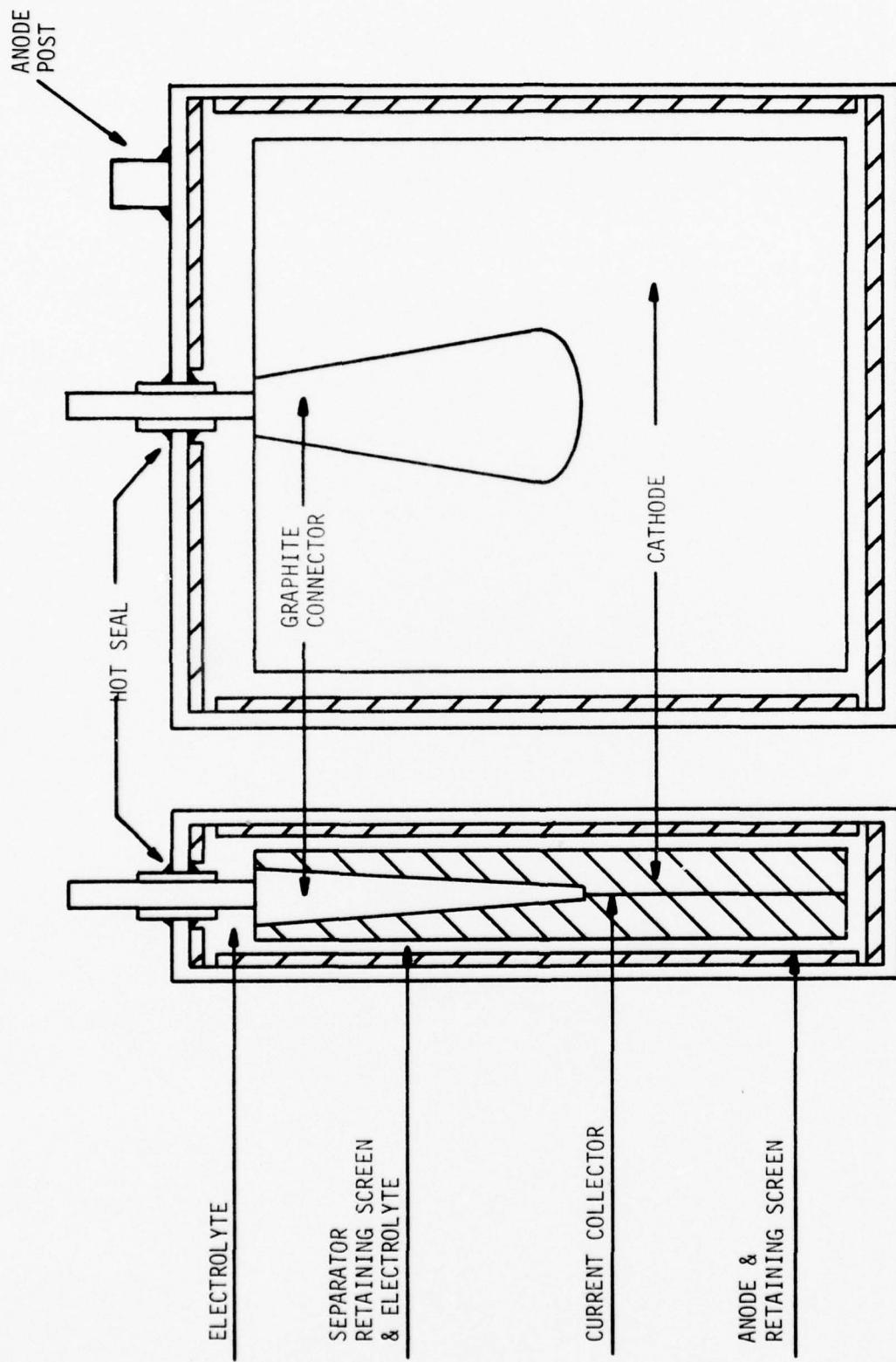
SCHEMATIC OF EARLY DESIGN MM-1 CELL WITH COLD SEAL

Figure 3



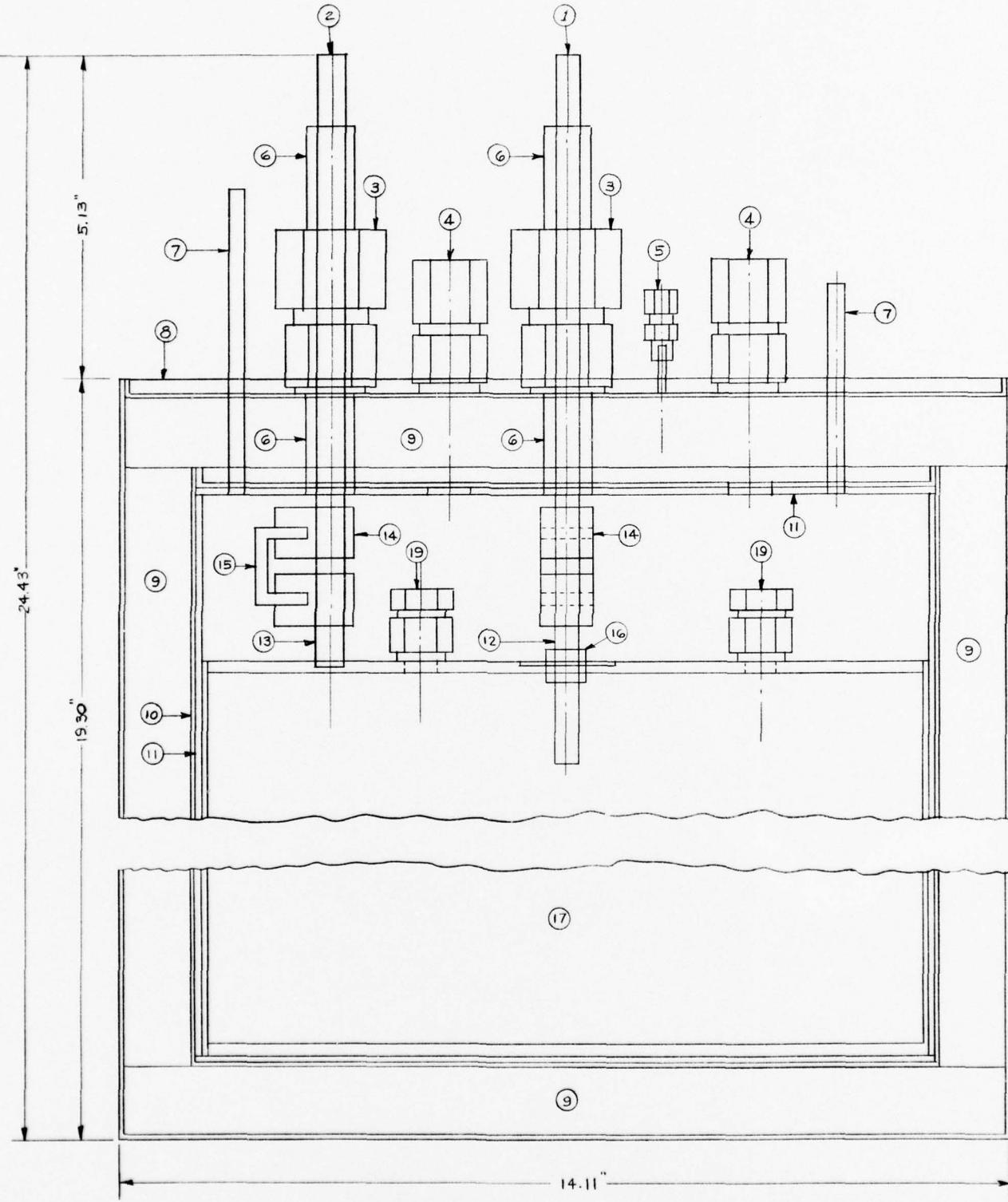
SCHEMATIC OF PRESENT DESIGN MM-1 CELL WITH COLD SEAL

Figure 4



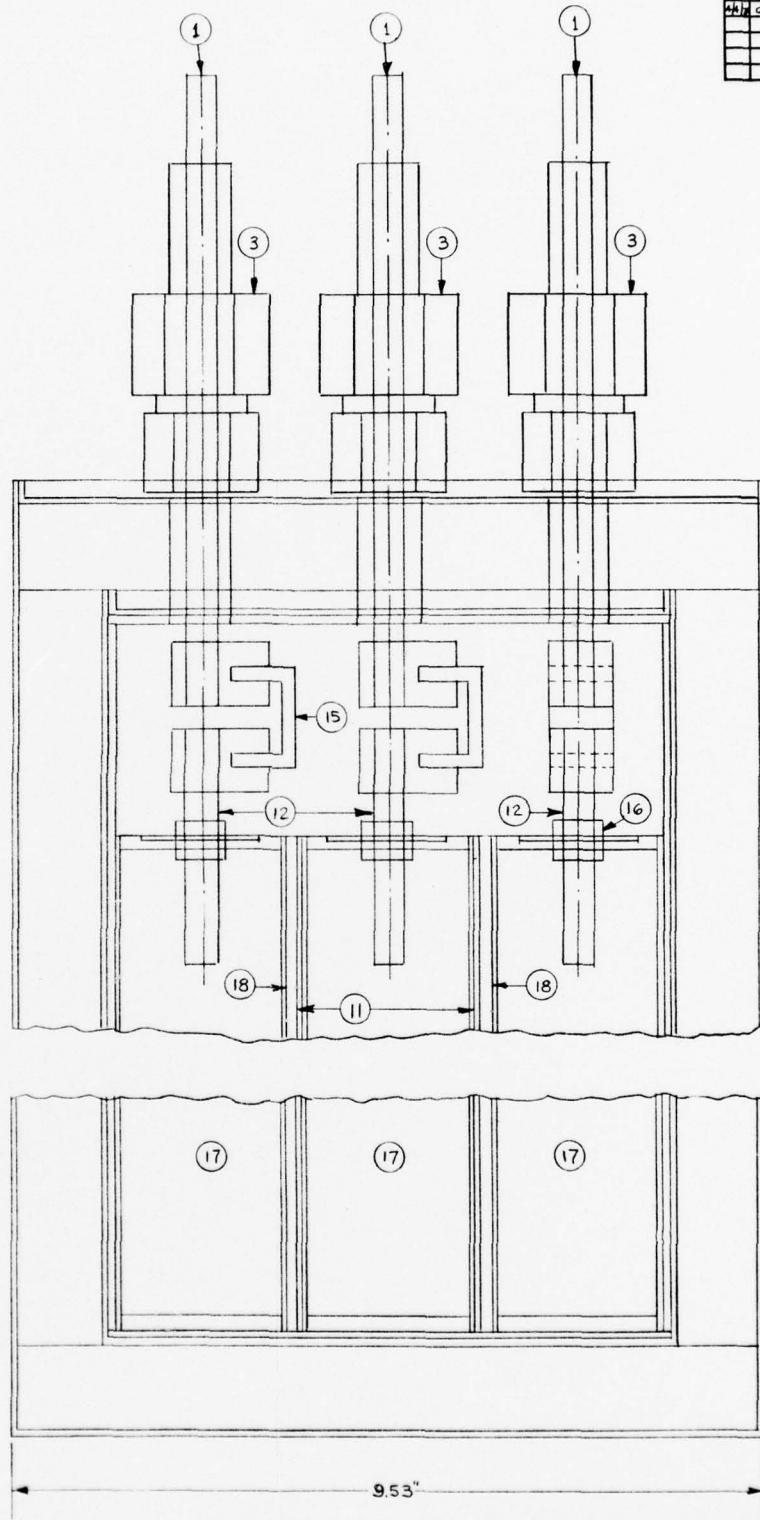
SCHEMATIC OF PRESENT DESIGN MM-1 CELL WITH HOT SEAL

Figure 5



NOTE - SEE DWG. NO. ESB-C105 FOR LEGEND

| DATE | BY | REVISION RECORD | AUTH | DR | CR |
|---------|----|----------------------|------|----|----|
| 4/17/81 | a | Redrawn without chgs | | | |



| | | |
|--|--|--|
| DESIGN/RELEASE APPROVALS APPROVED BY _____ DATE _____ | DRAWN BY R. E. B. DATE 8-17-77 CHECKED _____ SCALE NONE | ESB INCORPORATED TECHNOLOGY CENTER YARDLEY, PENNSYLVANIA |
| MATERIAL AS NOTED | | |
| DO NOT SCALE DRAWING | | |
| TOLERANCE | | |
| FRACTION | DECIMAL | ANGLES |
| ± 1/64 | XX ± 0.010 | XXX ± 0.005 |
| DRAWING NO. ESB-C102 D | | |

| DATE | REV. | REVISION RECORD | AUTH. DR. CL. |
|------|------|-----------------|---------------|
| | | | |
| | | | |
| | | | |
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| | | | |

LEGEND

- (1) Cathode Rod (Cu)
- (2) Anode Rod (Cu)
- (3) S/S Conax Gland EG-375-A-V
- (4) S/S Conax Gland MHC-062-A-2-V
- (5) S/S Conax Gland MPG-125-A-V
- (6) Alumina Insulator
- (7) 304 S/S tubing, $\frac{1}{4}$ " O.D.
- (8) S/S Outer Insulation Case, 219A.
- (9) Acetal Insulator (Min-K)
- (10) S/S Inner Insulation Case, 219A.
- (11) Electrical Insulation
- (12) Cell Cathode Rod (W)
- (13) Cell Anode Rod (Cs)
- (14) Copper Clamp
- (15) Copper Connector
- (16) Hot Seal
- (17) Cell
- (18) Heater
- (19) Swage lot. Cap

| | | |
|--------------------------|------------------------|-----------------|
| DESIGN/RELEASE APPROVALS | DRAWN BY <i>R.E.B.</i> | DATE 8-24-77 |
| APPROVED BY | CHECKED | SCALE |
| | | |
| | | |
| | | |
| DO NOT SCALE DRAWING | | |
| FRACTION | DECIMAL | ANGLES |
| $\pm 1/64$ | .XX ± .010 | $\pm 1/4^\circ$ |
| | XXX ± .008 | |

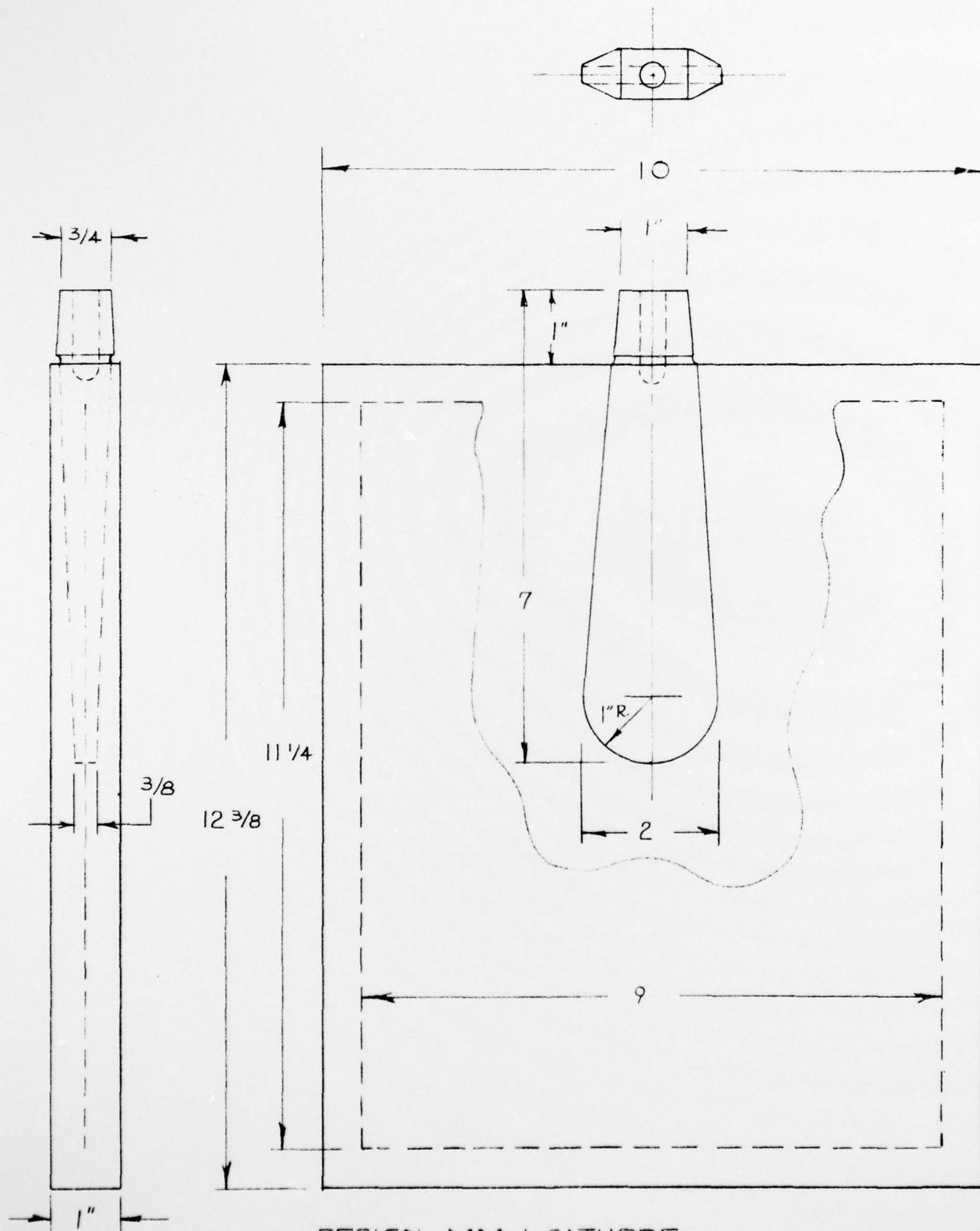
ESB INCORPORATED
TECHNOLOGY CENTER
YARDLEY, PENNSYLVANIA

LEGEND - 3 Cell//Battery Module

DRAWING NO. ESB-C105 **B**

Figure 6b

NOTE: BREAK ALL CORNERS



DESIGN MM-1 CATHODE

Figure 7

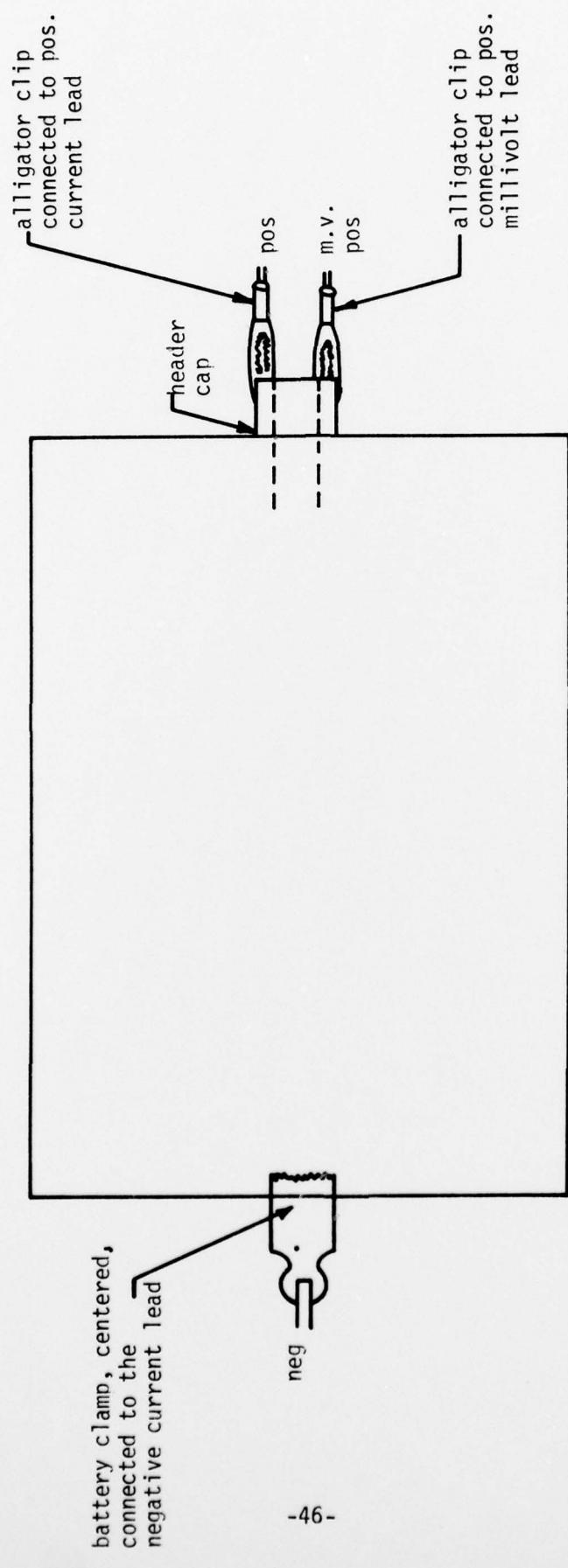
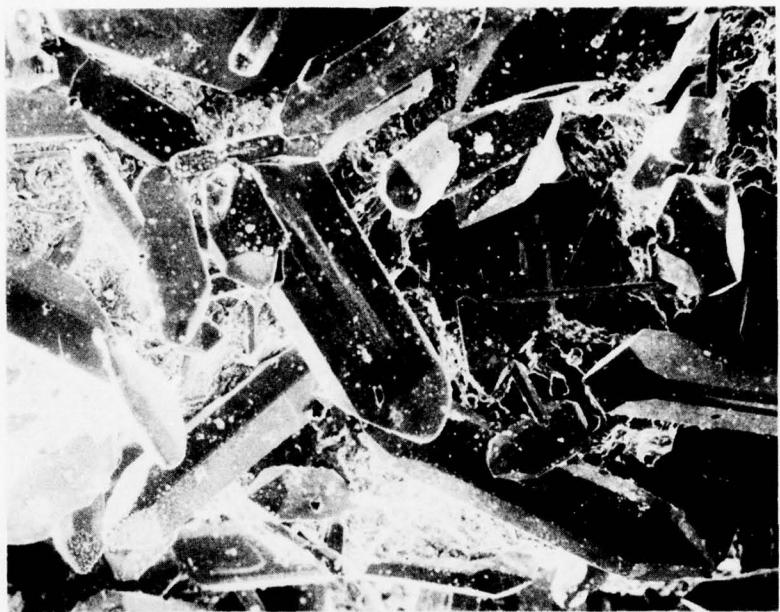


Figure 8 MILLIVOLT READING CONNECTION DIAGRAM

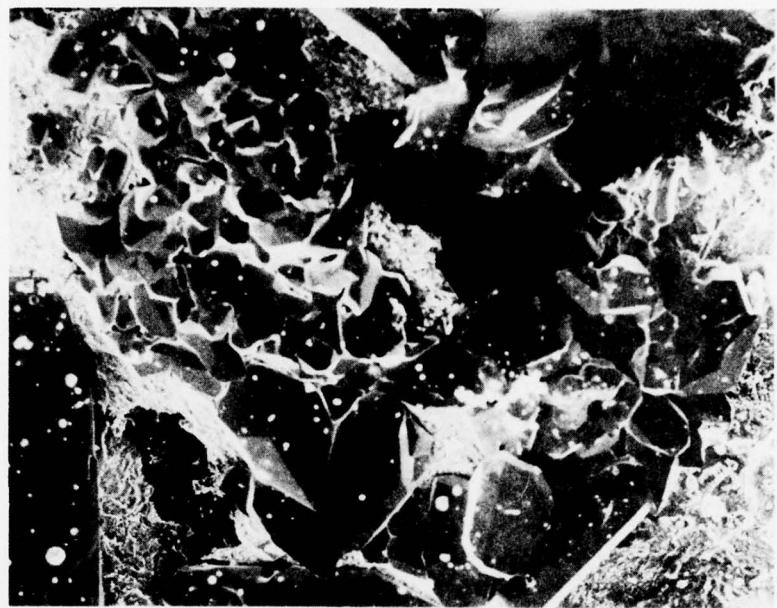


(a)



(b)

SEM PHOTOGRAPHS OF TELLURIUM (50 X)
(As Per A. Simon NRL)

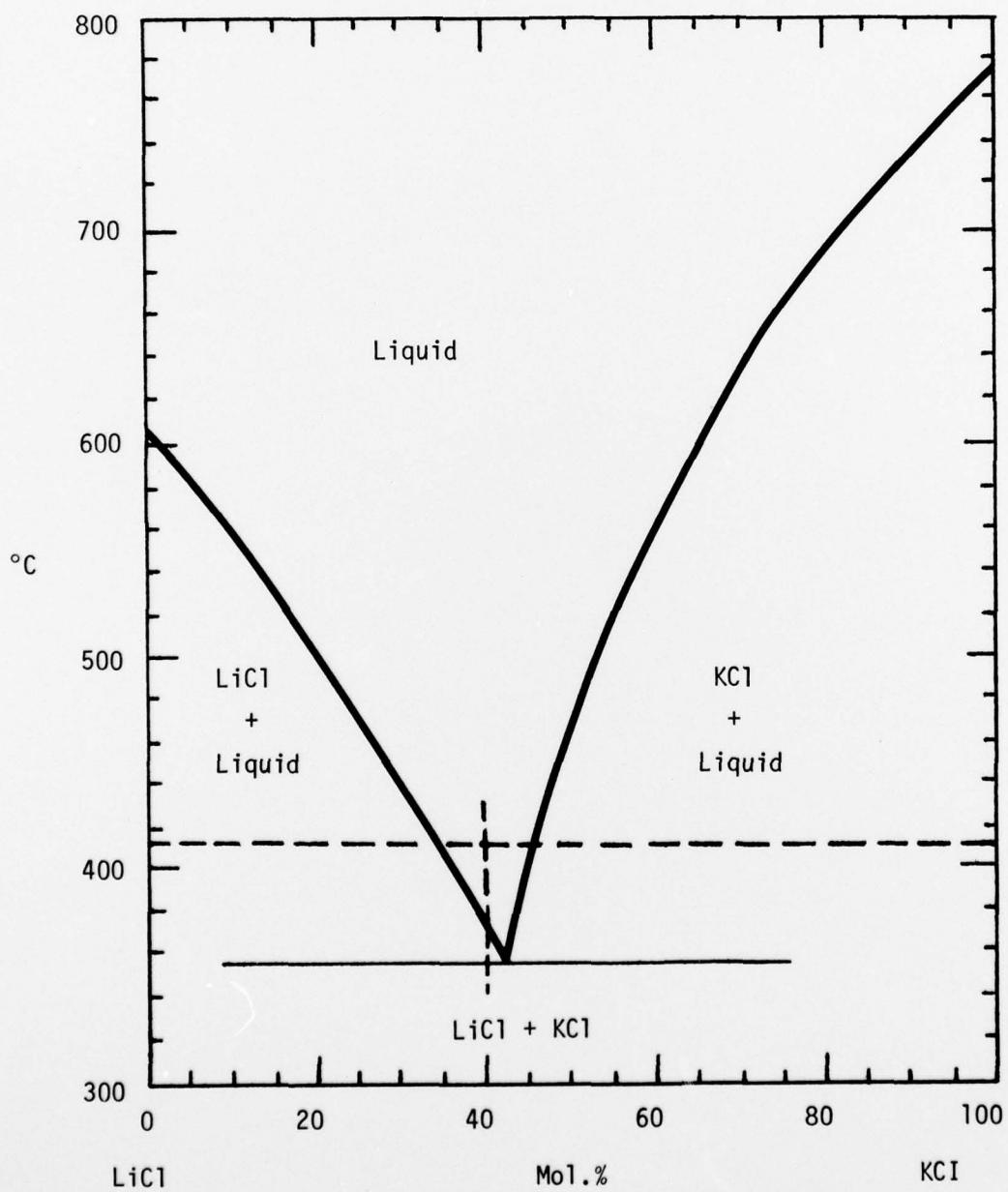


(a)



(b)

SEM PHOTOGRAPHS OF TELLURIUM (100X)
(As Per A. Simon NRL)



PHASE DIAGRAM OF THE LiCl-KCl System

Figure 11

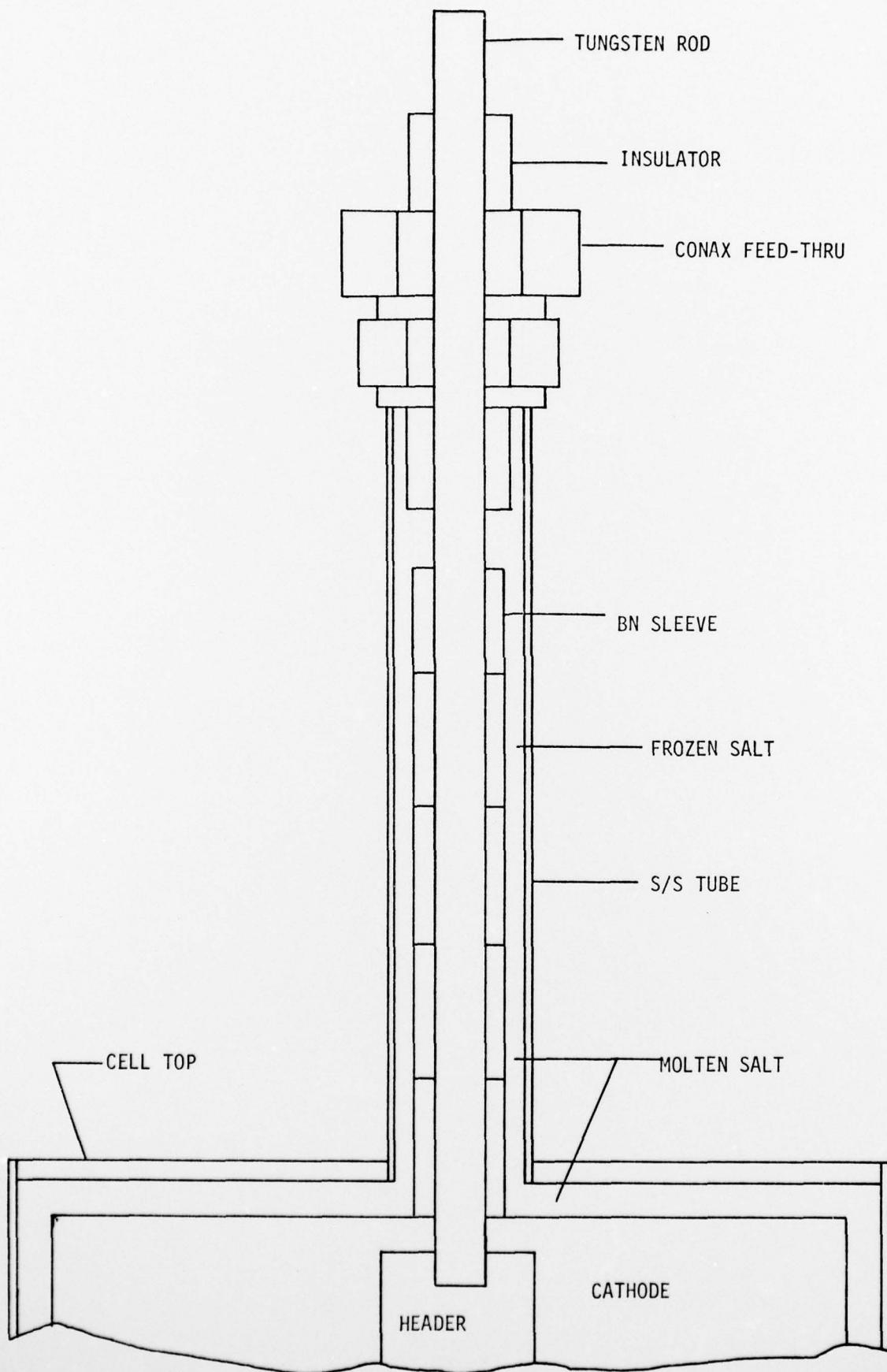


FIG 12 COLD SEAL

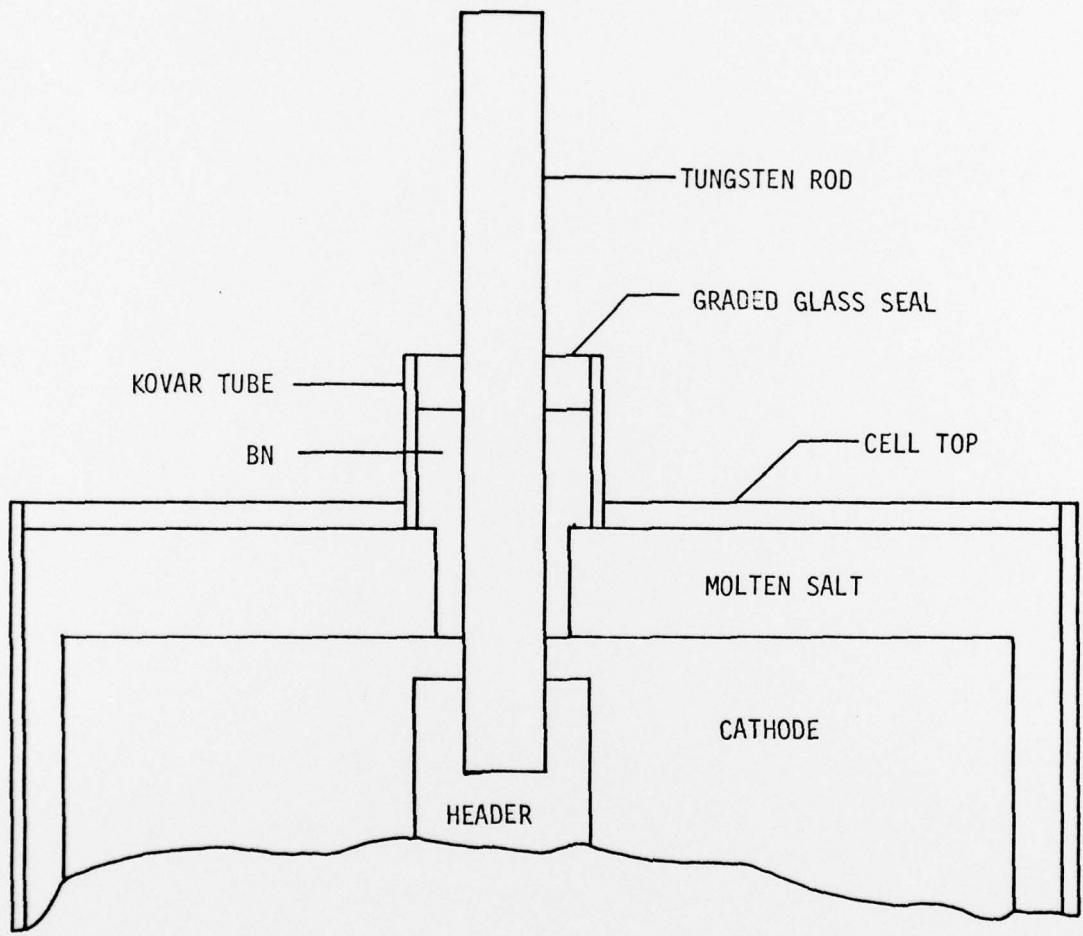
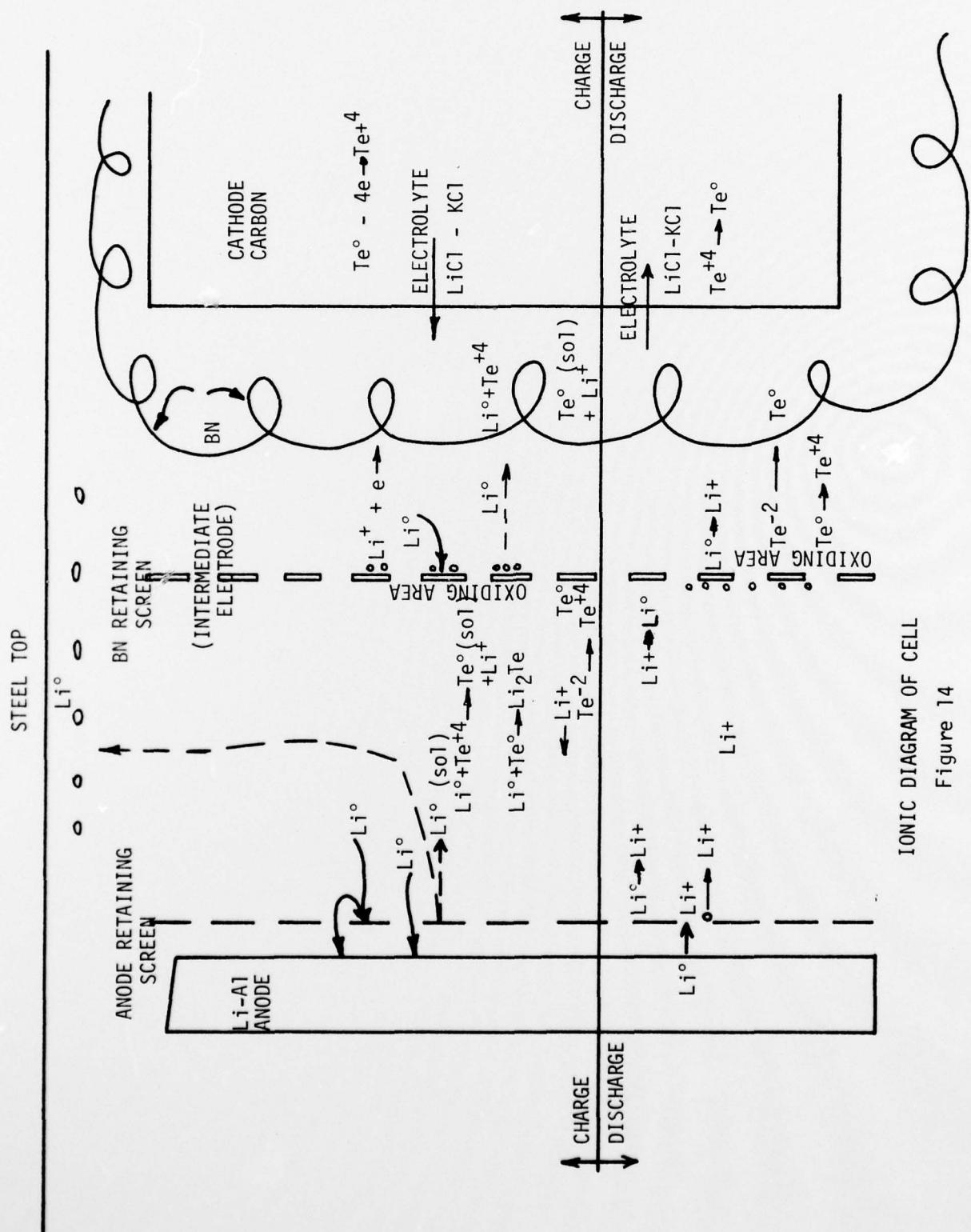


FIG 13 HOT SEAL



IONIC DIAGRAM OF CELL

Figure 14

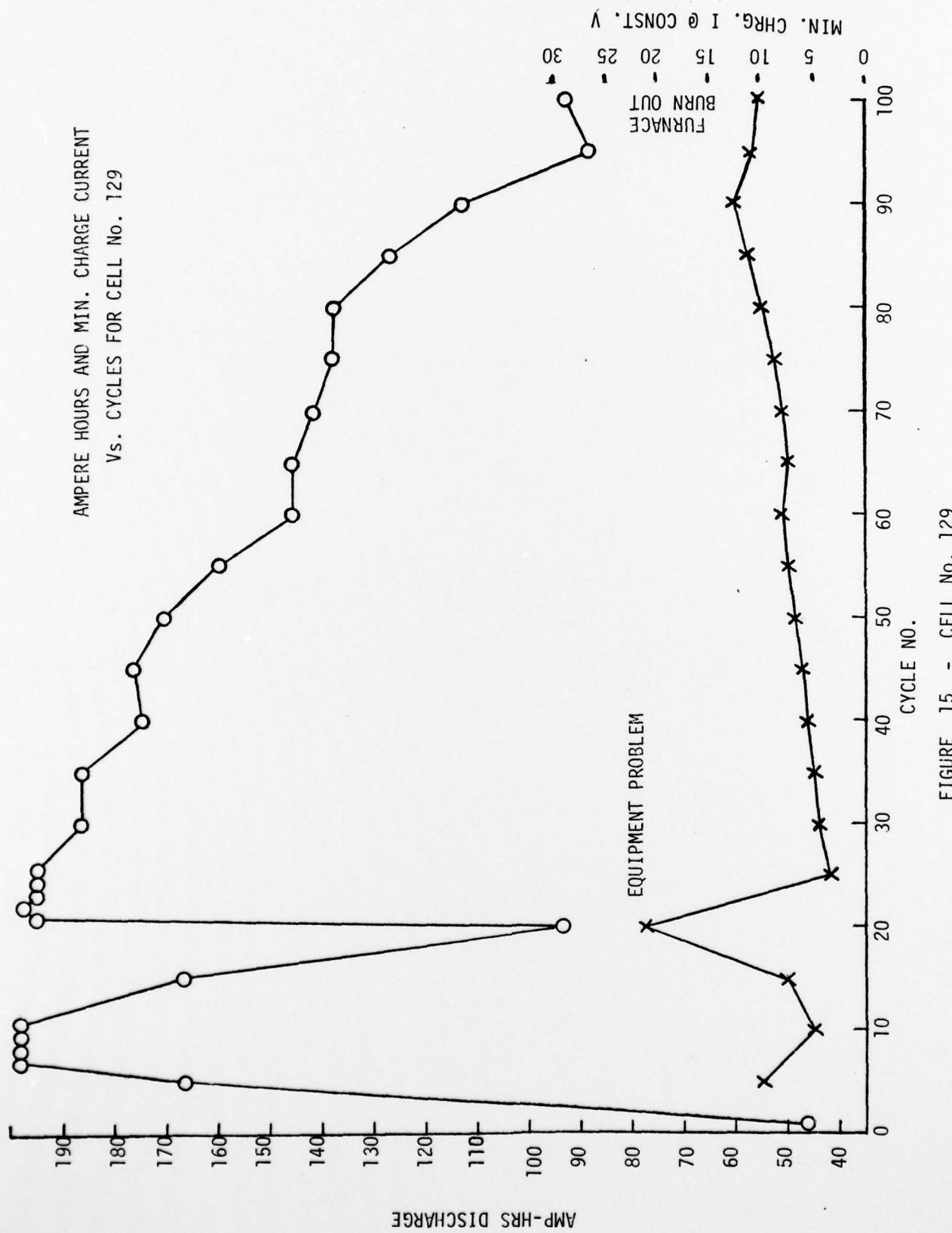


FIGURE 15 - CELL No. 129

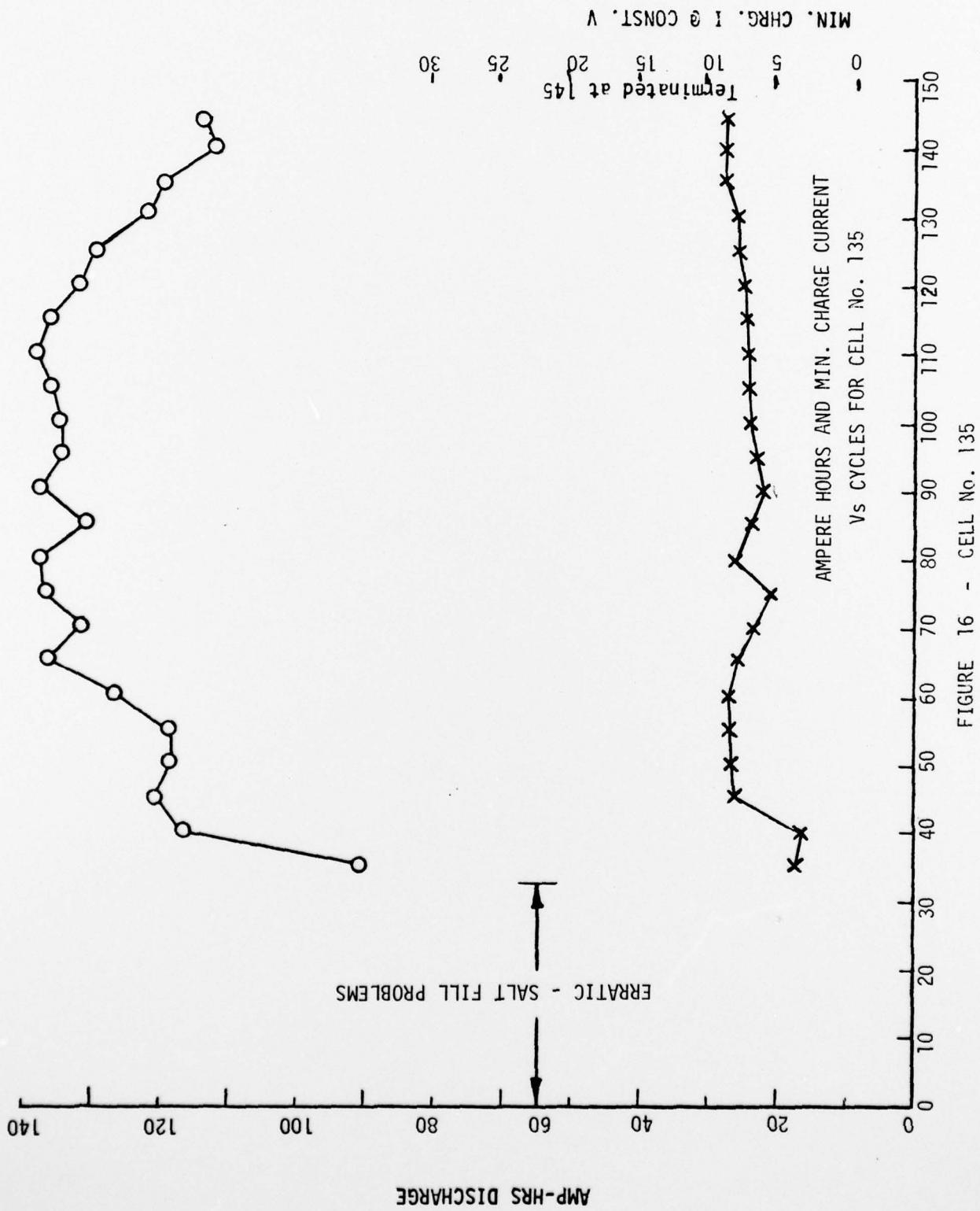


Figure 17 DIFFERENTIAL CAPACITANCE, CATHODE No. 464, Te Cl₄ TREATED

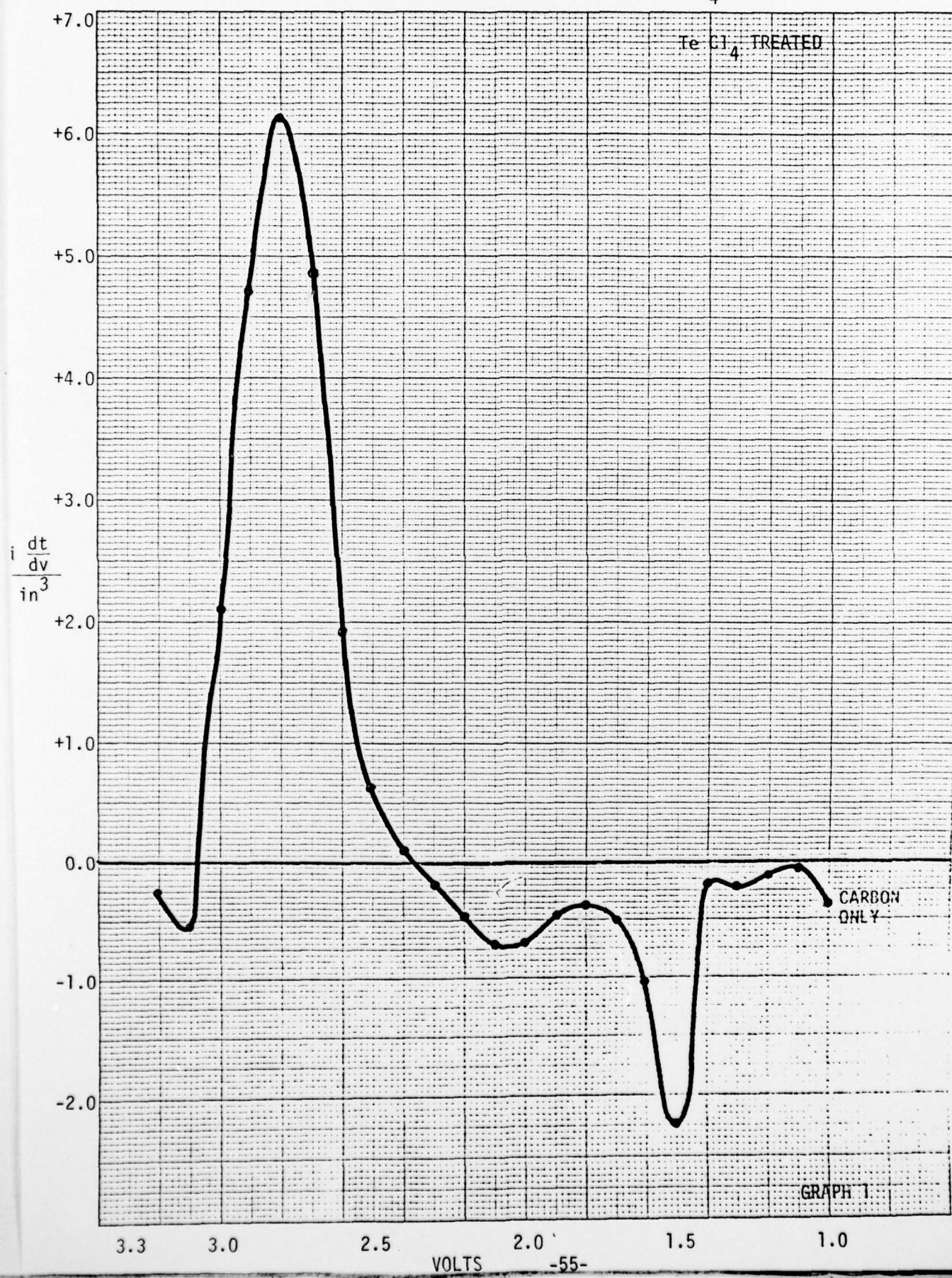
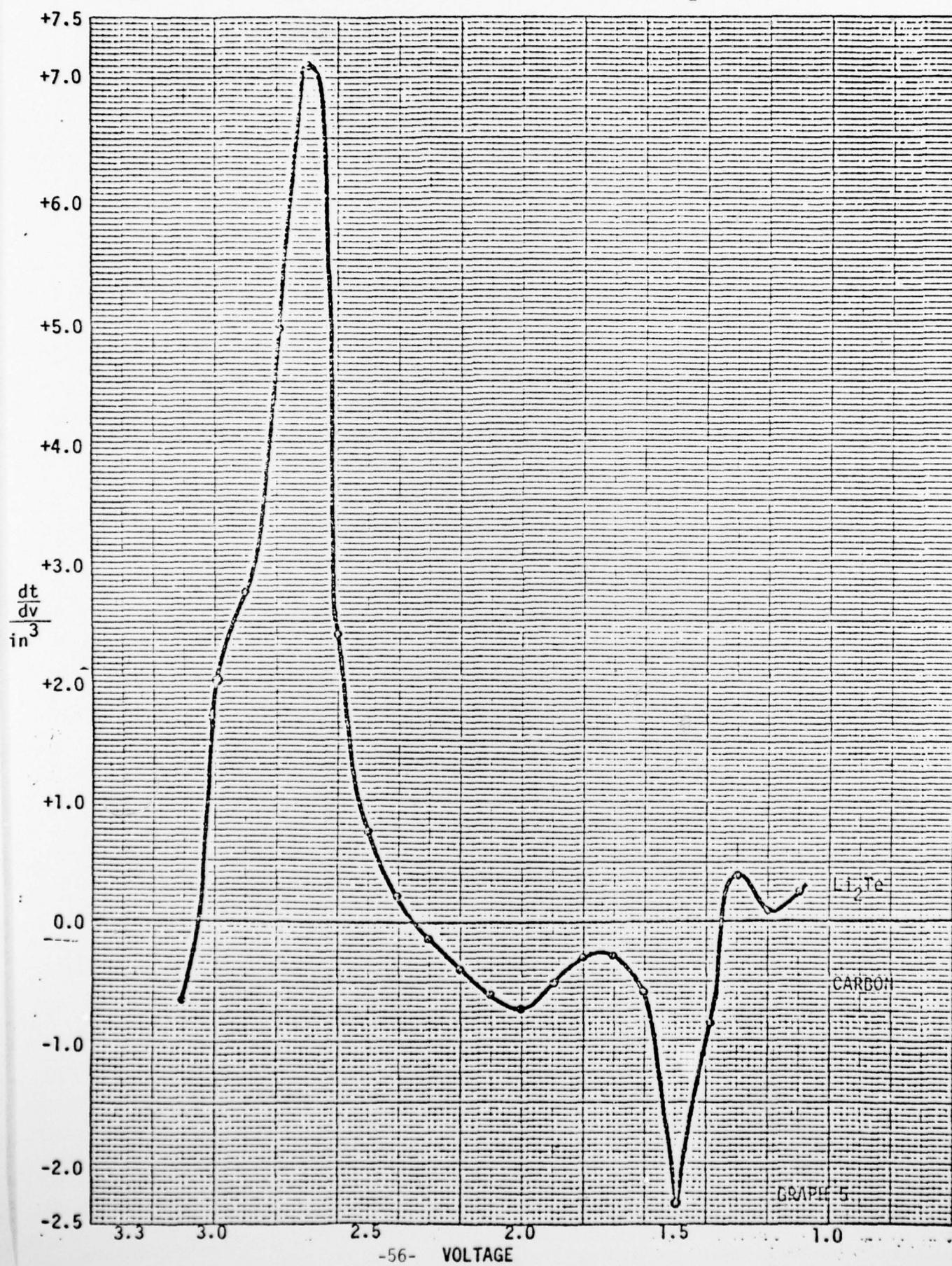


Figure 18 DIFFERENTIAL CAPACITANCE, CATHODE No. 468, Li₂Te TREATED



CARBON 464
 TeCl_4 TREATED

POT DESCRIPTION

F I
 II
 III
 IV

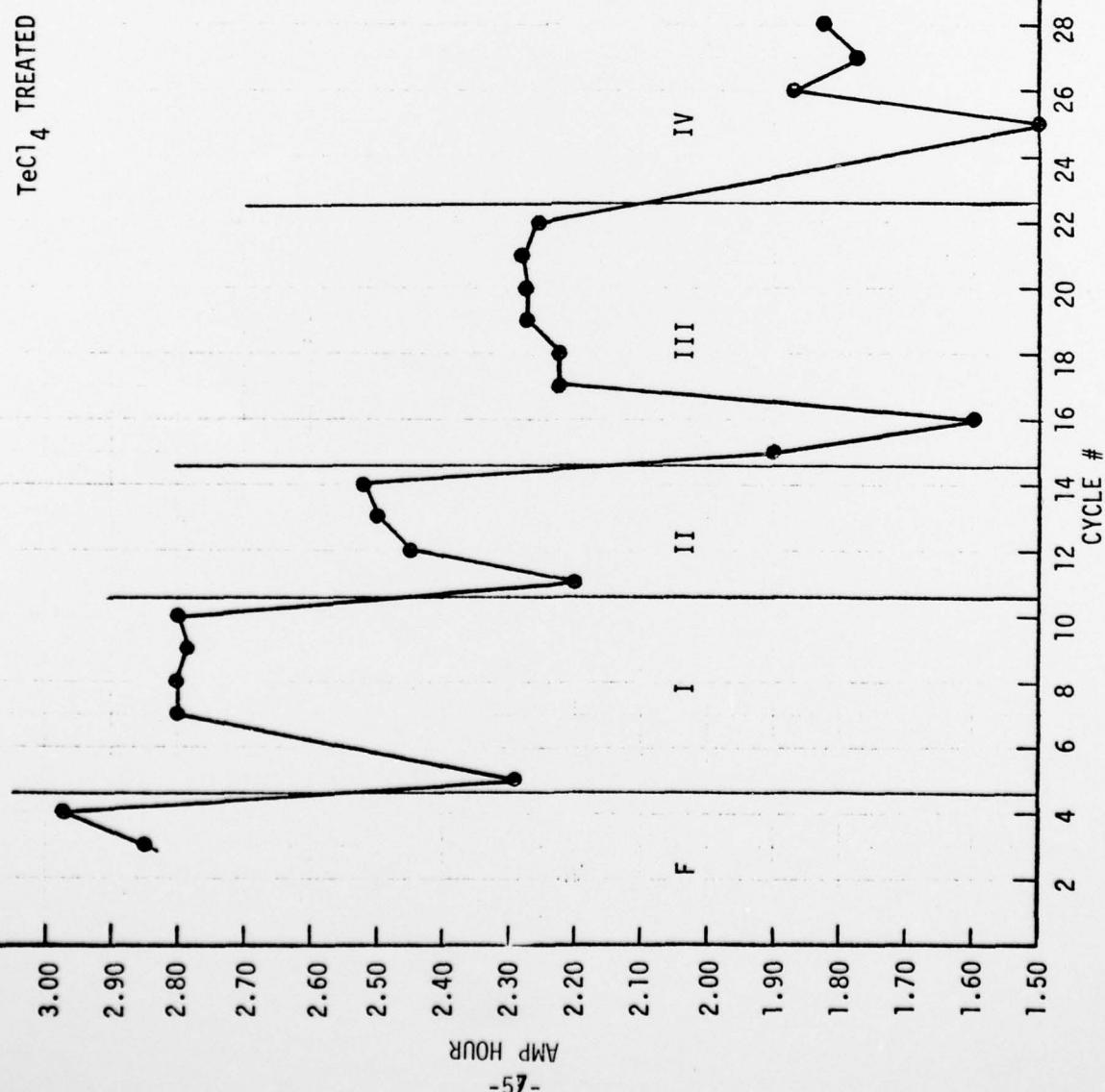


Figure 19 AH vs CYCLES, VIRGIN ELECTROLYTE

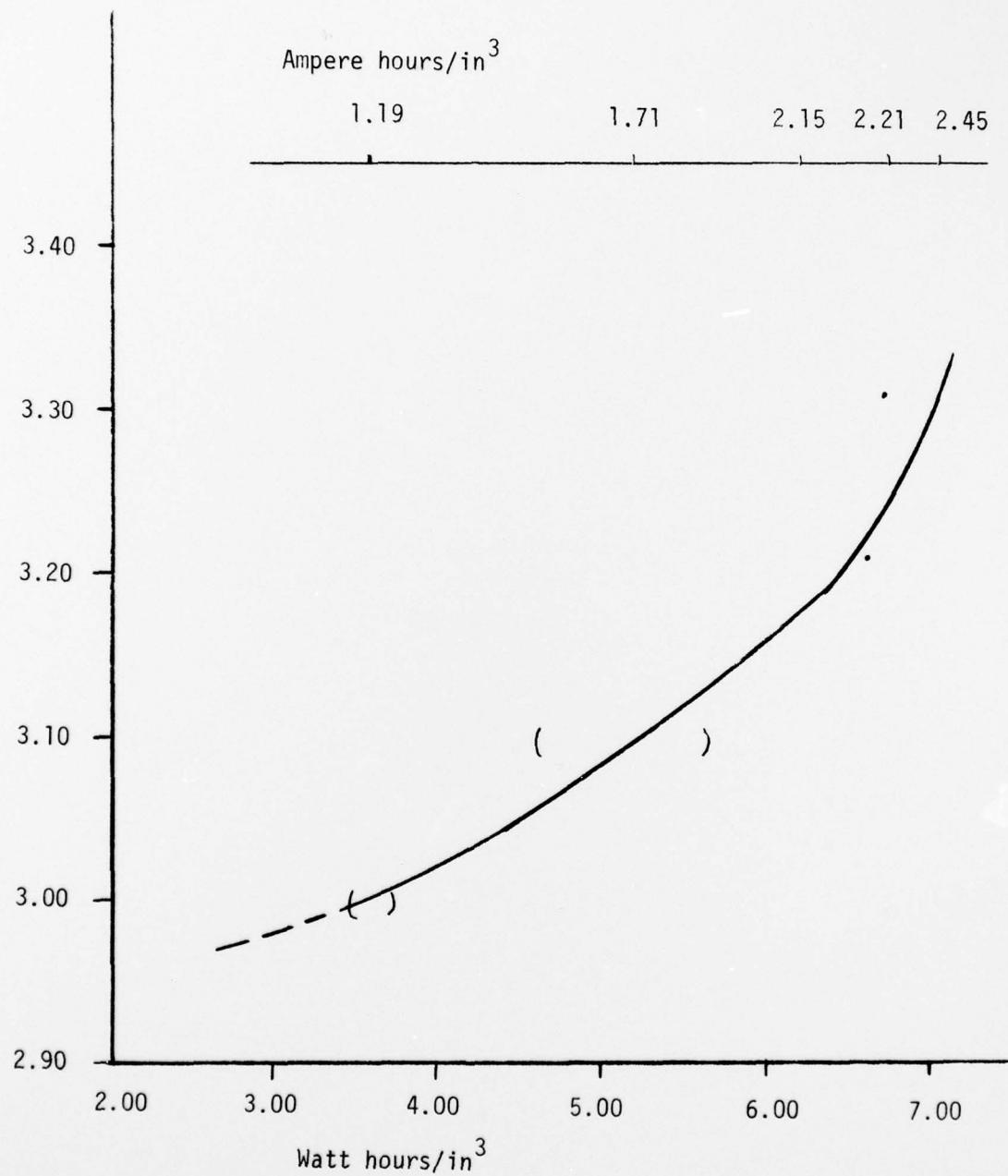


Figure 20 FINAL CHARGE VOLTAGE vs WH/in³